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OF THE

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VOLUME XVI.

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PROCEEDINGS

OF THE

Cambridge Philosophical Society.

The Determination of the Exponent to which a Number belongs, the Practical Solution of certain Congruences, and the Law of Quadratic Reciprocity. By H. C. POCKLINGTON, M.A., St John's College.

[*Received in revised form* 17 October 1910.]

1. In § 2 we describe a tentative process for finding the exponent to which a number belongs relative to a given prime, and also a modification of the direct process for solving some binomial congruences which greatly diminishes the labour when the modulus is a large prime. In § 3 we throw one of the known methods of solving $ax \equiv c \pmod{b}$ into the form of an algorithm, and show that it gives directly the least positive solution if a and c are numerically less than b (which will usually be the case); the method may also be used to solve $ax - by = c$. In § 4 we derive from a discussion of the linear indeterminate equation a simple proof of the second half of Gauss's third proof of the law of Quadratic Reciprocity.

2. If we wish to ascertain whether a number x is a primitive root of a given prime p the most convenient plan appears to be to raise x successively to the powers $(p-1)/p_1$, $(p-1)/p_2$, etc., where p_1, p_2, etc. are the different prime divisors of $p-1$. If one of these powers is congruent to unity, modulus p, then x is not a primitive root, and if none is congruent to unity we easily see that x is a primitive root. If we find that $x^m \equiv 1 \pmod{p}$, where m is some divisor of $p-1$, we may repeat the process, raising x to the powers m/p_1,

m/p_2, etc., where p_1, p_2, etc. are the different prime divisors of m, and it is clear that we shall at last find an index m such that $x^k \equiv 1$ if $k = m$ but not if k is any quotient of m by a prime occurring in it. It is easily seen that m is then the exponent to which x belongs.

To make this method effective we must have a ready means of raising x to a high power. The following method* is useful. First raise x to the powers 1, 2, 4, 8, etc. by successive squaring (with of course division by the modulus to find the least residue). Then express m as a sum of powers of 2 (i.e. express it in the binary scale) and multiply together the residues found for those powers that occur as terms in the value of m. Thus, to find the residue of x^{25} we multiply together the residues of x^{16}, x^8 and x itself. In this way we find without much trouble that the exponent of 3 to modulus 8191 is 910.

This last method can be used to facilitate the solution of the binomial congruence directly when this is possible (e.g. $x^2 \equiv a$ mod. p if $p = 4m + 3$ is prime, for a solution is $x \equiv a^{m+1}$). We notice that the labour required here is proportional to a power of the logarithm of the modulus, not to the modulus itself or its square root as in the indirect processes, and hence see that in the case of a large modulus the direct process will be much quicker than the indirect.

3. We often have to solve the linear congruence $ax \equiv c$ mod. b, or the indeterminate equation $ax - by = c$ which contains the congruence. The method commonly given is to convert b/a into a continued fraction, find the numerator and denominator of the penultimate convergent (the quickest way is to remove the last partial quotient and evaluate the fraction by ordinary arithmetic) and deduce a solution of the proposed equation by multiplying these by c. This method is perhaps the best if it does not matter which solution we find, but if we wish to find the least one (as is usually the case in solving a congruence) this method involves more work than that given below, which is simply a well-known process converted into an algorithm.

Changing the sign of one of the indeterminates if necessary, we write the equation in the form $a_2x_1 - a_1x_2 = b_2$, where a_1, a_2 are positive integers and $a_1 > a_2$, and b_2 is an integer. Let

$$a_1 = a_2d_2 + a_3, \quad b_2 = a_2e_2 - b_3,$$

where a_3, b_3 are positive integers (or zero) less than a_2 (i.e. a_3, b_3 are the positive and negative remainders of a_1 and b_2 respectively and d_2, e_2 the corresponding quotients, the divisor being a_2). Then we have $(a_3x_2 - b_3)/a_2 = x_1 - d_2x_2 - e_2 = x_3$ say, where x_3 is integral,

* It is a modification of one given, I believe in *Nature*, for the calculation of logarithms.

so that the equation is transformed into $a_3x_2 - a_2x_3 = b_3$. We repeat this transformation until we reach an equation

$$a_{n+1}x_n - a_nx_{n+1} = b_{n+1}$$

in which b_{n+1} is divisible by a_{n+1}, the quotient being e_{n+1}. Then a solution of this equation is $x_{n+1} = 0$, $x_n = e_{n+1}$ and we find solutions of the previous equations in turn by using the relation $x_{r-1} = d_rx_r + e_r + x_{r+1}$ until we reach the original equation.

Now let $r > 1$ and suppose that $0 \ngtr x_{r+1} < a_{r+1}$.

Then $$x_r = (b_{r+1} + a_rx_{r+1})/a_{r+1} \ngtr \{b_{r+1} + a_r(a_{r+1} - 1)\}/a_{r+1}$$
$$\ngtr a_r + (b_{r+1} - a_r)/a_{r+1}$$
$$< a_r, \text{ since } b_{r+1} < a_r.$$

Also $x_r \nless b_{r+1}/a_{r+1} > 0$, so that $0 < x_r < a_r$.

Hence, since the condition $0 \ngtr x_{n+1} < a_{n+1}$ is satisfied by x_{n+1}, the condition $0 < x_r < a_r$ is satisfied by all the other x's except x_1, and by x_1 also if $0 < b_2 < a_1$. It is satisfied by x_1 even when b_2 is negative if b_2 is numerically less than a_1 and x_2 is not zero, for then

$$x_1 = (b_2 + a_1x_2)/a_2 \nless (b_2 + a_1)/a_2 > 0.$$

If a_1 is prime to a_2 the different values of x_2 that satisfy the equation form an A.P. of constant difference a_2, and the only one of these that satisfies the inequality satisfied by the value found above is the least positive one. If a_1 is not prime to a_2 their greatest common divisor δ must divide b_2, otherwise the equation has no solution. Let $\alpha_1 = a_1/\delta$, $\alpha_2 = a_2/\delta$, $\beta_2 = b_2/\delta$, then we see that the numbers found for the d's and e's and hence for the x's are the same as for the equation $\alpha_2x_1 - \alpha_1x_2 = \beta_2$, so that the value found for x_2 is the least satisfying this equation, and hence also the least satisfying the original equation.

The arithmetical work may conveniently be arranged as shown in the example. Let it be required to solve the equation

$$79x_1 - 801x_2 = 673,$$

or the congruence $79x_1 \equiv 673 \pmod{801}$.

a	b	d	e	x
801				262
79	673	10	9	25
11	38	7	4	3
2	6	5	3	0

Place the numbers 801, 79, 673 as shown in the table. Divide 79 into 801, place the remainder below the 79 and the quotient

opposite the 79 in the third column. Divide 79 also into 673, place the difference between the remainder and the divisor below the dividend, and the quotient increased by unity opposite the divisor 79 in the fourth column, and proceed similarly till the divisor 2 divides the 6 that is opposite to it in the second column. The last column is worked upwards. Begin with zero, and above this place 3, the last number in the previous column. Multiply the 3 by the 7 that is opposite to it in the third column, and add on the two numbers nearest the 3, i.e. 4 and 0, which gives 25. Place this above the 3 and proceed. The last number found, 262, is the solution of the congruence, or $x_1 = 262$, $x_2 = 25$ is the solution of the equation.

4. The best known proof of the law of Quadratic Reciprocity for two odd primes p and q consists in first proving that

$$(p \mid q) = (-1)^{\lambda},$$

where λ is the number of solutions of $py \equiv -z \mod q$ subject to $0 < y < q/2$, $0 < z < q/2$, and then proving that $\lambda + \mu$ is even unless both p and q are of the form $4m+3$, when it is odd, where μ is what λ becomes when p and q are interchanged. The second half of this proof is far from neat in its original form, and the neatness of Eisenstein's proof may be questioned on the ground that it imports geometrical considerations. This part can however be proved easily by means of the indeterminate equation.

We have then λ equal to the number of solutions of

$$qx - py = z$$

subject to $0 < y < q/2$, $0 < z < q/2$. But this gives

$$x = (z + py)/q$$
$$\Rightarrow \{(q-1) + p(q-1)\}/2q \Rightarrow (p+1)/2 - (p+1)/2q < (p+1)/2,$$

so that $x < p/2$ since x is integral, and the equation shows that x is positive, so that $0 < x < p/2$. Also conversely if $0 < x < p/2$ and $0 < z < q/2$ we have

$$y = (qx - z)/p < qx/p < p/2$$

and

$$y > (2qx - q)/2p > q(2x-1)/2p > 0$$

for $x \not< 1$, so that $0 < y < q/2$. Hence the two sets of conditions are equivalent.

Hence λ is the number of solutions of $qx - py = z$ subject to $0 < x < p/2$, $0 < z < q/2$. But we also have μ equal to the number of solutions of $py - qx = -z$, i.e. of $qx - py = z$, subject to $0 < x < p/2$, $-p/2 < z < 0$. Hence $\lambda + \mu$ is the number of solutions of $qx - py = z$ subject to $0 < x < p/2$, $-p/2 < z < q/2$, for there is no solution when $z = 0$, $0 < x < p/2$.

But if we substitute for x, y, z, from

$$x + x' = (p+1)/2,\ y + y' = (q+1)/2,\ z + z' = (q-p)/2,$$

the equation transforms into $qx' - py' = z'$ subject to the conditions $\frac{1}{2} < x' < (p+1)/2$, that is $0 < x' < p/2$ since x is integral, and $-p/2 < z' < q/2$. The equation and conditions are the same as before. Hence the solutions are arranged in pairs, and their number is even, unless one solution is paired with itself, which requires $x = x'$, $y = y'$, $z = z'$. For this to hold we must be able to satisfy $2x = (p+1)/2$, $2y = (q+1)/2$, $2z = (q-p)/2$, so that p and q must be of the form $4m+3$. If they are, this self-paired solution exists, and the number $\lambda + \mu$ of solutions is odd. But $(p \mid q)(q \mid p) = (-1)^{\lambda+\mu}$ and so is $+1$ if $\lambda + \mu$ is even and -1 if $\lambda + \mu$ is odd. Hence $(p \mid q)(q \mid p) = +1$ unless p and q are both of the form $4m+3$, and then it equals -1, which is the law of Quadratic Reciprocity. The quadratic character of 2 is easily determined by finding directly the number of solutions of $2x \equiv -z \mod p$ subject to $0 < x < p/2$, $0 < z < p/2$.

The Divisors of certain Arithmetical Forms, the Primes of certain Forms, and the Arrangement of Quadratic and some other Residues. By H. C. POCKLINGTON, M.A., St John's College.

[*Received in revised form* 17 October 1910.]

1. In § 2 we find a condition that $x^n \pm y^n$ may be a prime, and deduce that all primes of the form $2^n + 1$ are Fermat's primes, finding also some primitive roots of these primes. In §§ 3—5 we show that on certain conditions the divisors of $[x^n - y^n]$ are of the form $mn + 1$, and in § 6 we prove the converse. In § 7 we show that the number of primes of the form $mn + 1$ is infinite, that the number not of this form is infinite if $n > 2$, and that the number not of either of the forms $mn \pm 1$ is infinite if $n = 5$ or > 6, where n is any given number. In § 8 we show how to find any number of primes that are quadratic residues of each other and discuss the irregularity of determinants of quadratic forms. In § 9 we show that every number is a quadratic residue of an infinite number of primes, and, if not a square, also a non-residue of an infinite number, and apply the result to the theory of quadratic forms. In § 10 the number of primes within any given limits is found in terms of an integral containing known functions only. In §§ 11, 12 we give a discussion of the form of the prime divisors of $mx^2 + ny^2$ by elementary methods, and in § 13 extend it to the case of $ax^2 + 2bxy + cy^2$, the divisors not being restricted to be prime. In §§ 14, 15 we discuss the arrangement of quadratic, cubic and biquadratic residues and also quadratic non-residues, and in § 16 we apply the results to prove the possibility of certain congruences and to the representation of a number as the sum of four squares (the representation as the sum of three squares is also considered). We also here find a formula for the number of solutions of any congruence.

2. In discussing the arithmetical divisibility of the number $U = x^n - y^n$, where $n > 1$, we notice first that the expression can be split into algebraical factors. As the coefficients of these factors are integers, each algebraical factor is an arithmetical divisor also. Since $x - y$ is always a factor and is $< x^n - y^n$, we see that U is not a prime unless $x - y = 1$. Also if e is a divisor of n other than n itself and $f = n/e$, then $U = (x^e)^f - (y^e)^f$ and $x^e - y^e$ is a factor. This cannot be unity or U itself. Hence U can only be a prime when $x = y + 1$ and n is prime. In particular $2^n - 1$ is not a prime if n is composite. If n is prime $2^n - 1$ is called a Mersenne's number.

Next consider $U = x^n + y^n$. If n has an odd divisor f other than unity and $e = n/f$, then U has a factor $x^e + y^e$ which cannot be unity or U itself (unless $x = y = 1$, which we exclude in what follows). But the only numbers that have no odd divisor other than unity are the powers of 2. Hence U can only be a prime when n is a power of 2. It is clearly further necessary that x and y should have no common divisor and that one should be even and the other odd. In particular the odd prime numbers of parts into which a circle can be divided by ruler and compasses, which are prime numbers of the form $2^n + 1$, are all of the form $2^{2^n} + 1$, and hence are Fermat's primes. They are

3, 5, 17, 257, 65537, etc.

Again, if we proceed to find the common factor of

$$(x^m - 1)/(x - 1) \text{ and } (x^n - 1)/(x - 1)$$

by algebra, we find that when m is prime to n the last remainder is unity. Hence they have no common factor and if x is integral have no common divisor. Hence no two of Mersenne's numbers have any common divisor. Similarly $x^m + 1$ and $x^n + 1$, where m and n are powers of 2, give on division a remainder 2, so that no two of Fermat's numbers have a common divisor. In the same way we see that no Mersenne's number can have a common divisor with a Fermat's number.

In dividing the circle into $p = 2^n + 1$ parts when p is prime, or in solving the equation $x^p - 1 = 0$, we must know a primitive root of $x^{p-1} \equiv 1 \text{ mod. } p$. Now any non-primitive root of this congruence belongs to an exponent that is a submultiple of $p - 1$ and so a power of 2. Hence the exponent divides $(p-1)/2$ and the root must be a quadratic residue. Hence any quadratic non-residue must be a primitive root. Now since p is of the form $4m + 1$ we have

$$\left(\frac{3}{p}\right) = \left(\frac{p}{3}\right) = \left(\frac{(-1)^n + 1}{3}\right) = \left(\frac{2}{3}\right) = -1,$$

so that 3 is a primitive root. The other primitive roots are the first $(p-1)/2$ odd powers of 3. The proof does not apply if $p = 3$, in which case the only primitive root is 2. In the same way we can prove that 5 and 10 are primitive roots except when $p = 5$ and $p = 3$ or 5 respectively.

3. We now consider the form of the divisors of the integral expression $(x^n - y^n)/(x - y)$, where n is a prime and x prime to y. Let p be a prime divisor of this expression, and first let p not divide $x - y$. It is clear that p does not divide x or y, and hence from Fermat's theorem $x^{p-1} \equiv y^{p-1} \text{ mod. } p$. Also by hypothesis $x^n \equiv y^n \text{ mod. } p$. Let r be the lowest index for which $x^r \equiv y^r$

mod. p. Then r is not unity, for the congruence $x \equiv y$ is not satisfied. Now all the indices for which the congruence holds are multiples of r. Hence n is a multiple of r, and as it is prime we have $r = n$. Also $p - 1$ is a multiple of r and hence of n. Let it be mn. Then $p = mn + 1$.

Next let p divide $x - y$ as well as $(x^n - y^n)/(x - y)$. Then since

$$(x^n - y^n)/(x - y) = ny^{n-1} + n(n-1)\, y^{n-2}(x-y)/2 + (x-y)^2 U,$$

we have ny^{n-1} also divisible by p, and hence n is divisible by p since y is not. Hence $p = n$. We see further that

$$(x^n - y^n)/(x - y)$$

is not divisible by n^2. Moreover the product of any number of numbers of the form $mn + 1$ is of the same form. Collecting the results we have the following theorem, viz.: $(x^n - y^n)/(x - y)$ is divisible only by numbers of the form $mn + 1$ unless $(x - y)$ is divisible by n, and then the expression is divisible only by n and numbers of the forms $n(mn + 1)$ and $mn + 1$. In particular, all the divisors of the Mersenne's number $2^n - 1$ are of the form $mn + 1$, and the number being odd its divisors are odd, so that m is even, and so the divisors are of the form $2mn + 1$, a result due to Fermat.

4. We now take n to be composite. Let $[x^n - y^n]$ denote the algebraical prime factor of $x^n - y^n$, let p be a prime divisor of $[x^n - y^n]$ and first let it not divide any algebraical factor $x^e - y^e$ of $x^n - y^n$. As before we have $x^n \equiv y^n$, $x^{p-1} \equiv y^{p-1}$ mod. p, and if r is the least index for which $x^r \equiv y^r$ mod. p, we have $r = n$, for r must be n or some submultiple of n, and it is not the latter for then we should have $x^e - y^e$ divisible by p when $e = r$. Hence we again find that $p - 1$ is divisible by n and have the result that p is of the form $mn + 1$.

Next if p divides one of the algebraical factors of $x^n - y^n$, say $x^e - y^e$, as well as $[x^n - y^n]$, it also divides $(x^n - y^n)/(x^e - y^e)$, for this expression contains $[x^n - y^n]$ as a factor. But if $f = n/e$,

$$(x^n - y^n)/(x^e - y^e) = (x^e - y^e)(x^{n-2e} + 2x^{n-3e} y^e + \ldots) + fy^{n-e}.$$

Hence as p does not divide y it divides f and therefore n. Hence $x^n - y^n$ is not prime to n.

Collecting results and extending to the case of a composite divisor as before we have the theorem: Any divisor of $[x^n - y^n]$ that is prime to n is of the form $mn + 1$; and if $x^n - y^n$ is prime to n, all the divisors of $[x^n - y^n]$ are of the form $mn + 1$.

5. The case of $x^n + y^n$ when n is a power of 2 and x is prime to y is contained in the last result, for $x^n + y^n = [x^{2n} - y^{2n}]$. However, on account of the importance and great simplicity of this

case, it may perhaps be discussed separately. If p is an odd prime divisor of $x^n + y^n$ we have $x^n \equiv -y^n$, $x^{p-1} \equiv y^{p-1}$ mod. p, and if r is the least index for which $x^r \equiv -y^r$ mod. p, then the other indices for which this congruence holds are odd multiples of r. But a power of 2 is an odd multiple of no number but itself. Hence $r = n$. Also the indices ρ for which $x^\rho \equiv y^\rho$ are even multiples of r and hence of n, so that $p-1$ is an even multiple of n, and $p = 2mn+1$, a result due to Euler.

In particular, all the divisors of a Fermat's number $2^{2^n}+1$ are of the form $m2^{n+1}+1$.

If $2^n = \lambda(n+1)+\mu$ we find the remainder on dividing $m2^{n+1}+1$ into the Fermat's number to be a power of 2 multiplied by $2^\mu + (-1)^\lambda m^\lambda$, which must be divisible by $m2^{n+1}+1$ if the Fermat's number is.

6. Conversely, every prime p of the form $mn+1$ is a divisor of some number of the form $[a^n-1]$. For since n is a divisor of $p-1$, the congruence $x^n \equiv 1$ mod. p has n solutions, and at least one of these (g^m if g is a primitive root of $x^{p-1} \equiv 1$ mod. p) is such that $x^r \equiv 1$ mod. p is not true for any index less than n. Let a be such a root. Then p divides a^n-1 and does not divide any algebraical factor a^e-1 of this expression, hence it divides the prime factor $[a^n-1]$.

In particular, all primes of forms $3m+1$, $4m+1$ divide numbers of the forms a^2+ab+b^2 and a^2+b^2 respectively.

7. There are some primes of the form $mn+1$, for the prime divisors of $[(na)^n-1]$ are all of this form as $(na)^n-1$ is prime to n, and every number other than unity has a prime divisor (itself if no other).

Now let any number of such primes be taken and let N be their product. Then any prime divisor of $[(nN)^n-1]$ is of the form $mn+1$, for $(nN)^n-1$ is prime to n, and it is not included among the primes taken, for they are prime to $(nN)^n-1$ and hence to $[(nN)^n-1]$. Hence if we know any number of primes of the form $mn+1$ we can always find another, so that the number of such primes is infinite.

The number of primes not of this form is also infinite if $n>2$. For there obviously are some. Let N be the product of any number of such primes. Then $nN-1$ is not of the form $mn+1$, hence it has at least one prime divisor that is not of the form $mn+1$, and this is not included among those taken to form N, for none of those divide $nN-1$. Hence we have added one prime at least to those taken, and as before we conclude that the number of such primes is infinite.

Similarly, taking r a prime* less than $n-1$ and prime to n

* We take r to be any prime divisor of $n-1$ unless this is prime, and if it is, any odd prime divisor of $n-2$ or $n+2$, for these are not both powers of 2 if $n>6$.

and putting N equal to the product of primes not of the forms $mn \pm 1$, excluding r, we find by considering $nN + r$ that the number of primes not of either of the forms $mn \pm 1$ is infinite if n is 5 or greater than 6.

In particular, there are an infinite number of primes of each of the forms $3m+1$, $3m+2$, $4m+1$, $4m+3$, $6m+1$, $6m+5$.

Again, let N be the product of any number of primes of the form $8m+3$. The N^2+2 is divisible only by numbers of the form x^2+2y^2 and therefore of the forms $8m+1$ and $8m+3$. And being itself of the form $8m+3$ it has at least one prime divisor of this form. This is not one of those taken to form N, and hence as before the number of primes of the form $8m+3$ is infinite.

Similarly, by discussing $8N^2-1$, which is divisible only by primes of which 2 is a quadratic residue, i.e. primes of the forms $8m \pm 1$, at least one of which is of the form $8m-1$, we find that the number of primes of the form $8m+7$ is infinite.

Taking the form N^2+2^2, and remembering that N is odd, we see that the prime divisors are of the forms $8m+1$ and $8m+5$, and one at least is of the latter form. Hence the number of primes of the form $8m+5$ is infinite.

Again, $5N^2-1$ is divisible only by primes of the forms $5m \pm 1$, and one at least is of the form $5m-1$, hence the number of primes of this form is infinite.

Collecting the more interesting results, we have shown the existence of an infinite number of primes of each of the forms $3m+1$, $3m+2$, $(4m+1, 4m+3)$, $5m+1$, $5m \pm 2$, $5m+4$, $(6m+1, 6m+5)$, $8m+1$, $8m+3$, $8m+5$, $8m+7$.

8. We can find any number of primes that are quadratic residues of each other. For take any prime p_1 and find a prime p_2 of the form $4mp_1+1$, then find a prime p_3 of the form

$$4m'p_1p_2+1, \text{ etc.}$$

We have seen that each step is possible in an infinite number of ways and it is clear that each prime is a quadratic residue of those that precede it, and from the law of quadratic reciprocity it follows immediately that each prime is a quadratic residue of all the others*.

Hence the binary quadratic forms of determinant

$$D = -p_1p_2p_3 \dots p_n$$

contain 2^{n-1} ambiguous classes in the principal genus, and as there is no limit to n there is none to the number of bases required to express the principal genus by composition or to the index of irregularity. The same result can also be got by taking

$$D = -p_1^2p_2^2 \dots,$$

* Such primes are most easily found by trial. We find that a set is 3, 13, 61, 601, 757.

where $p_1, p_2 \ldots$ are any primes. For example if

$$D = -2^2 . 3^2 . 5^2 . 7^2 . 11^2 = -5336100$$

there are 16 ambiguous classes in the principal genus. One base may be taken to be (169, 33, 31581), the period of which is 12, and the others may be seven of the ambiguous classes. The index of irregularity is 8.

The case of $D = -297675 = -3^5 . 5^2 . 7^2$ is interesting, for $-D$ can be expressed four times in the form $m^2(8km + 3)$. By comparing with the determinant -3 we find the number of classes in the principal genus to be 81. We may take as bases the forms (4, 1, 74419), (9, 3, 33076), (25, 10, 11911), (49, 21, 6084), each of which belongs to the exponent 3, and by compounding we find the 81 classes. Hence the index of irregularity is 27.

9. The number $\pm x$ is a quadratic residue of all primes of the form $4mx + 1$. Hence every positive or negative number is a quadratic residue of an infinite number of primes. We proceed to show that unless it is a positive square it is also a non-residue of an infinite number of primes. First let the number be negative and equal $-x$, then, using Jacobi's extension of Legendre's symbol, we have $(-x \mid y) = -1$, where y is

$$4m - 1,\ 8m - 1,\ 4m - 1,\ 4m - 1,\ 8m - 3 \text{ or } 4m - 5,$$

according as x is

$$4m,\ 8m + 1,\ 8m + 2,\ 4m + 3,\ 8m + 5 \text{ or } 8m + 6,$$

provided that y is positive, and hence $-x$ is a non-residue of at least one prime divisor of y. The cases excluded because y is to be positive are those of 1, 2, 3, 5, 6 and 14 taken negatively, and these numbers are non-residues of 3, 5, 5, 11, 13 and 11 respectively. Hence every negative number is a quadratic non-residue of some prime, which in general is numerically less than the number, and never numerically exceeds the number by more than 7.

Next let the number be positive and equal x, and let $x = 4^\alpha u$, where u is not divisible by 4, then the quadratic characters of x and u with respect to any odd prime are the same, hence

$$(x \mid y) = (u \mid y) = -1$$

when u is $\quad 8m + 2,\ 8m + 3,\ 8m + 6$ or $8m + 7$,

y being taken to be

$$4m + 3,\ 8m - 5,\ 4m + 11 \text{ or } 8m + 5$$

respectively, provided that y is positive, and hence x is a non-residue of at least one prime divisor of y. The excepted case is that of $u = 3$ and 3 is a non-residue of 5. The prime thus found is less than x unless x is 2, 3 or 6, and is never greater than $x + 2$.

If u is of the form $4m+1$ let the different primes dividing u be p_1, p_2, p_3, etc. Since u is not a square, one at least of these, say p_1, occurs to an odd power in u. Let b be a non-residue of p_1 and let the congruences

$$v \equiv b \text{ mod. } p_1, \quad v \equiv 1 \text{ mod. } p_2, \quad v \equiv 1 \text{ mod. } p_3, \text{ etc.}$$

be solved to find a value of v that is positive and less than $p_1, p_2, p_3, \ldots$ and hence $< u$. Then $(v \mid u) = -1$ and $(u-v \mid u) = -1$. Hence taking y to be that one of v and $u-v$ that is odd, we have $(x \mid y) = (u \mid y) = (y \mid u) = -1$ and so x is a non-residue of at least one prime divisor of y. The prime thus found is always less than x. Hence every positive and not square number is a quadratic non-residue of some prime, which in general is less than the number, and never exceeds the number by more than 2.

Hence if x is any number that is not a square we can find a prime p_1 of which it is a non-residue, then a prime p_2 of which xp_1^2 is a non-residue, then a prime of which $xp_1^2p_2^2$ is a non-residue, and so on without limit. These primes are clearly different, and x is a non-residue of each, which proves the theorem enunciated above.

If two determinants D_1, D_2 of binary quadratic forms are such that every number prime to D_1D_2 that can be represented by some form of either can also be represented by some form of the other, then the character of D_2 with respect to any prime that does not divide D_1D_2 is the same as that of D_1. Hence D_1D_2 is a quadratic residue of every such prime, and so is a square. Hence D_1 and D_2 are in the ratio of two squares. We see immediately that this condition is sufficient as well as necessary.

10. We conclude our discussion of the numbers of primes of various forms by finding a formula for the number of primes between given limits. Let $\phi(x)$ and $\psi(x)$ be any one-valued functions of x that vanish for all positive integral values of x, and are real, finite and not zero for all other positive values of x. Let $F(x) = \{\phi(x)\}^2 + \left\{\psi\left(\frac{1+\Gamma(x)}{x}\right)\right\}^2$ and suppose $x > 1$. In order that $F(x)$ may vanish, each of the squares composing it must vanish. The first vanishes when and only when x is an integer and the second when the argument of ψ is integral. But, x being integral, this happens when and only when x is prime (since $x > 1$), as we see from Wilson's theorem. Hence the necessary and sufficient condition for the vanishing of $F(x)$ is that x should be a prime, and the number of primes between given limits is equal to the number of roots of $F(x)$ between these limits. The simplest form of $F(x)$ is got by taking

$$\phi(x) = \psi(x) = \sin \pi x,$$

ut we may also use the reciprocal of the Gamma-function of egative argument. The roots are in any case double ones; if ve secure that they are not of any higher order of multiplicity, heir number is given by the complex integral

$$\frac{1}{4\pi i}\int dx F'(x)/F(x)$$

aken round a contour including the part of the real axis between he limits but not including any complex root. The discussion of he integral presents much difficulty. If we replace $\phi(x)$ by $\phi\left(\frac{x-b}{a}\right)$ we have a formula for the number of primes of the form $na+b$.

We can also use Wilson's theorem to find a series for the number of primes. Let n be an integer greater than 4, then $u_n = \tan \pi (n-1)!/n$ vanishes if n is not prime, and is $-\tan \pi/n$ if n is prime, and is less than 1 since $n > 4$. Hence the series

$$-u_n + u_n^3/3 - u_n^5/5 + \text{etc. ad inf.}$$

s zero if n is not prime and converges to the value π/n if n is prime. Hence the sum

$$\sum_{n=a+1}^{n=b-1} n\,(-u_n + u_n^3/3 - u_n^5/5 + \ldots \text{ ad inf.})/\pi$$

s equal to the number of primes between a and b, provided that > 3. This formula seems as intractable as the other.

11. We shall require the following lemma, viz.:

If m, n, A, B, D are any numbers, and

$$kA = \lambda D + \lambda', \; kB = \mu D + \mu',$$

ve can find a value of k satisfying $0 < k \not> 2\sqrt{(N/3)}$ such that $n\lambda'^2 + n\mu'^2 < D^2$, where $N = mn$.

Write θ for the greatest integer in $2\sqrt{(N/3)}$ and let all the esidues (not merely the least positive residues) λ', μ' of kA and kB be taken for each value of k within the limits and represented by points on a plane having Cartesian coordinates $\lambda'\sqrt{m}$, $\mu'\sqrt{n}$, nd let circles be drawn of diameter D and with their centres at hese points. Also let circles of the same diameter be drawn with centres at the points whose coordinates are multiples of $D\sqrt{m}$ and $D\sqrt{n}$ respectively. Then for the whole of the plane the number f circles per unit area is $(1+\theta)/D^2\sqrt{mn}$. But the largest number of such circles that can be drawn per unit area without overlapping is

$$2/D^2\sqrt{3} = 2\sqrt{(N/3)}/D^2\sqrt{mn} < (1+\theta)/D^2\sqrt{mn}.$$

Hence some circles must overlap. If one of the first set overlaps one of the second set, we take the value of k corresponding to this

circle. If two of the first set overlap and the corresponding values of k are k_1 and k_2, we take $k_1 \sim k_2$ as our value for k. The corresponding residues are numerically equal to $\lambda_1' - \lambda_2'$ and $\mu_1' - \mu_2'$ and satisfy the inequality in question.

12. If mx is prime to ny, and $mn = N$ contains no square factor, then every prime divisor of $mx^2 + ny^2$ is either within the limits assigned to k or of the form $(m'u^2 + n'v^2)\, k$, where $m'n' = mn = N$ and $0 < k \not> 2\sqrt{(N/3)}$ in either case, and also $m'u$ is prime to $n'v$.

For if not, let p be a prime that does not satisfy the conditions of the hypothesis and divides some number of the given form, and let $mx^2 + ny^2$ be the least such number that p divides (subject to $mn = N$). Then $x \not> p/2$ for otherwise either

$$m(x-p)^2 + ny^2 \text{ or } m(p-x)^2 + ny^2$$

is of the given form, divisible by p and less than $mx^2 + ny^2$, which is contrary to the assumption. For the same reason $y \not> p/2$.

Now put
$$kpx = \lambda(mx^2 + ny^2) + \lambda' \quad \ldots\ldots\ldots\ldots\ldots\ldots(1),$$
$$kpy = \mu(mx^2 + ny^2) + \mu' \quad \ldots\ldots\ldots\ldots\ldots\ldots(2),$$

where k satisfies the given inequalities for k and

$$m\lambda'^2 + n\mu'^2 < (mx^2 + ny^2)^2.$$

If $\lambda' = 0$ we have $kpx = \lambda(mx^2 + ny^2)$ and x is prime to $mx^2 + ny^2$, hence it divides λ. Let $\lambda/x = \lambda''$, then

$$kp = \lambda''(mx^2 + ny^2).$$

Now p divides $mx^2 + ny^2$ and hence is not greater than it. Hence $\lambda'' \not> k < p$ for by hypothesis p is greater than the upper limit assigned to the numbers k.

Hence λ'' is prime to p and so divides k. If the quotient is k' we have $p = (mx^2 + ny^2)/k'$, where $0 < k' \not> 2\sqrt{(N/3)}$, which is contrary to the assumption as to the form of p. Hence λ' is not zero, and similarly we can prove that μ' is not zero.

We now consider the number

$$(m\lambda^2 + n\mu^2)(mx^2 + ny^2) = (m\lambda x + n\mu y)^2 + N(\mu y - \lambda x)^2,$$

which is obviously an integer divisible by p. Substituting for λ and μ their values from (1) and (2) this expression becomes

$$\left(kp - \frac{m\lambda' x + n\mu' y}{mx^2 + ny^2}\right)^2 + N\left(\frac{\mu' x - \lambda' y}{mx^2 + ny^2}\right)^2,$$

where the terms in each bracket are the same as before and so integral. Hence

$$\left(\frac{m\lambda' x + n\mu' y}{mx^2 + ny^2}\right)^2 + N\left(\frac{\mu' x - \lambda' y}{mx^2 + ny^2}\right)^2 = A^2 + NB^2 \text{ say}$$

s divisible by p. If now

$$A = (m\lambda' x + n\mu' y)/(mx^2 + ny^2)$$

s zero we change the sign in each bracket, which is equivalent o conducting the multiplication in the other of the two ways. 'hen A' is not zero, and

$$B' = (\mu' x + \lambda' y)/(mx^2 + ny^2) = (mx^2 - ny^2)/mx\,(mx^2 + ny^2)$$

s not zero, for mx is prime to ny. If B is zero we proceed in the ame way.

Hence, supposing the signs to have been changed if necessary, e can say that neither A nor B is zero.

Now $(\mu' x - \lambda' y)^2 = (\lambda'^2 + \mu'^2)(x^2 - y^2) - (\lambda x + \mu y)^2$

$$\not> (\lambda'^2 + \mu'^2)\, p^2/2, \text{ since } x \not> p/2,\ y \not> p/2,$$

$$\not> (m\lambda'^2 + n\mu'^2)\, p^2/2,$$

hence $$B \not> (m\lambda'^2 + n\mu'^2)^{\frac{1}{2}}/(mx^2 + ny^2) < p,$$

nce $m\lambda'^2 + n\mu'^2 < (mx^2 + ny^2)^2$. Hence p is not a common divisor f A and B, so that if A_1, B_1 are the quotients of A, B by their ommon divisor, $A_1^2 + NB_1^2$ is divisible by p. Now remove the ommon divisor of A_1 and N. Since N is not divisible by p (for and n are not) the resulting expression, say $m'A_2^2 + n'B_2^2$, where $'n' = N$, is divisible by p. Now

$$m'A_2^2 + n'B_2^2 \not> A^2 + NB^2 \not> (m\lambda'^2 + n\mu'^2)/(mx^2 + ny^2) < mx^2 + ny^2.$$

ence we have found an expression of the form $mx^2 + ny^2$, where x is prime to ny and $mn = N$, which is divisible by p and is less an the least such expression, which is absurd. Hence we con- ude that the theorem enunciated at the head of this section is ue. We note that k must satisfy the further condition that mn is a quadratic residue of k in order that k may be capable of viding $m'u^2 + n'v^2$.

This proof of the theorem is long and does not apply to com- osite divisors, and is given mainly because it involves nothing ut elementary considerations and because it may be possible to tend it to the analogous case of the divisibility of x or y by p hen xy is divisible by p, where x, y and p are complex numbers mposed with the nth roots of unity and p is prime.

13. Let $U = ax^2 + 2bxy + cy^2$, where x is prime to y, be visible by any number δ, and let the determinant of the form D. Then $\Omega^2 \equiv D$ can be solved for modulus U and therefore modulus δ, so that δ satisfies the necessary and sufficient con- tion for being capable of primitive representation in some form determinant D. In fact, if we find λ and μ such that

$$\mu x - \lambda y = 1,$$

then $(a\lambda^2 + 2b\lambda\mu + c\mu^2)(ax^2 + 2bxy + cy^2)$
$$= \{a\lambda x + b(\lambda y + \mu x) + c\mu y\}^2 + ac - b^2 = \Omega^2 - D$$
is divisible by δ, and hence the form
$$\left(\delta,\ \Omega,\ \frac{\Omega^2 - D}{\delta}\right)$$
has its coefficients integers, and it obviously can represent δ. The form is properly primitive if δ is prime to $2D$.

If the reduced form is (α, β, γ) we have
$$\delta = \{(\alpha u + \beta v)^2 - Dv^2\}/\alpha,$$
where $\alpha \not> 2\sqrt{(-D/3)}$ if D is negative, and $< \sqrt{D}$ if D is positive. We can easily deduce the result of § 12 if δ is a prime number prime to D. In particular, any divisor of $x^2 + y^2$ is of the form $u^2 + v^2$, and any divisor of $x^2 + 6y^2$ or $3x^2 + 2y^2$ is of one of the forms $u^2 + 6v^2$ or $3u^2 + 2v^2$, where in each case the terms are to be prime to each other.

14. We know that if p is a prime of the form $4m + 1$ then $p = \alpha^2 + \beta^2$, where α is odd and β even, and also from a theorem due to Gauss* that $2\alpha \equiv 2m!/m!\,m!$ mod. p, if the sign of α is so chosen that $\alpha \equiv 1$ mod. 4. But we have† $\Sigma x^r \equiv 0$ mod. p, where the summation extends to all values of x satisfying $0 < x < p$, unless r is divisible by $p - 1$, and then $\Sigma x^r \equiv -1$. Hence
$$\Sigma (x^3 - \lambda x)^{2m} \equiv (-\lambda)^m \,.\, 2m!/m!\,m!.$$
If then $\lambda = a$, where a is any quadratic residue of p, so that $\lambda^m \equiv \pm 1$ mod. p, we have $\pm 2\alpha \equiv \Sigma Qx\,(x^2 - a)$, where Qu means the quadratic character of u, that is $(u \mid p)$, and is taken to be zero if u is divisible by p. Now two terms under the Σ vanish, for there are two solutions of the congruence $x^2 - a \equiv 0$ mod. p, so that the number of terms is even. Hence $\pm\alpha \equiv \Sigma Qx\,(x^2 - a)$. But each side of this congruence is numerically less than $p/2$, so that we can replace the sign of congruence by that of equality and get $\alpha = \pm \frac{1}{2}\Sigma Qx\,(x^2 - a)$ or $\alpha = \pm \Sigma Qx\,(x^2 - a)$, where x in the last equation is subject to $0 < x < p/2$. If we put $a = 1$ this takes the simpler form $\alpha = \pm \Sigma Q\,(x - 1)\,x\,(x + 1)$.

If we now put $\lambda = b$, where b is any quadratic non-residue, we have $2\beta' = \Sigma Qx\,(x^2 - b) = \pm 2b^m\alpha$ and hence
$$4(\beta'^2 + \alpha^2) \equiv 4(1 + b^{2m})\,\alpha^2 \equiv 0 \text{ mod. } p,$$
whence $\beta' \equiv \pm\beta$, and as before we can change this to an equality and get $\beta = \pm \frac{1}{2}\Sigma Qx\,(x^2 - b)$, where $0 < x < p$, or $\beta = \pm \Sigma Qx\,(x^2 - b)$, where $0 < x < p/2$.

* H. J. S. Smith, B.A., *Rep.* 1863 (Newcastle-on-Tyne), p. 772. The other theorems of a similar character quoted below are also from this place.

† If γ is a primitive root the series is $\Sigma\gamma^{r\sigma}$ and on summing this geometrical progression we get the result stated.

If we now substitute in the equation $p = \alpha^2 + \beta^2$ remembering hat the formulae for α and β contain $(p-3)/2$ and $(p-1)/2$ erms respectively, we get

$$p = (p-3)/2 + (p-1)/2 + 2\Sigma Qxy\,(x^2-a)\,(y^2-a) + 2\Sigma Qxy\,(x^2-b)\,(y^2-b),$$

hich gives the curious result

$$\Sigma Qxy\,(x^2-a)\,(y^2-a) + \Sigma Qxy\,(x^2-b)\,(y^2-b) = 1,$$

here the summations extend to all values of x and y satisfying $< x < p/2$, $x < y < p/2$. If we could prove this result directly e should have a new proof that $p = \alpha^2 + \beta^2$.

Similarly if $p = 8m+1 = \alpha^2 + 2\beta^2$ we can use the congruence $2\alpha \equiv 4m!/m!\,3m!$ and find that $\alpha = \pm\frac{1}{2}\,\Sigma Qx\,(x^4+1)$, where

$$0 < x < p/2.$$

15. If we arrange the numbers from 1 to $p-1$ in order and stinguish the quadratic residues, we find that they are arranged groups containing one or more numbers and separated by non-sidues, e.g. in the case of $p = 13$ the numbers are

$$1,\ (2),\ 3,\ 4,\ (5),\ (6),\ (7),\ (8),\ 9,\ 10,\ (11),\ 12,$$

here we have two groups of one and two groups of two residues. the number of these groups is N, the number of residues eceded by a non-residue is $N-1$ for the first group of residues preceded by zero, which is not a non-residue.

Hence $4(N-1)+2 \equiv \Sigma\,\{1-(x^2-1)^{\frac{1}{2}(p-1)}\}$, where $0 < x < p$, r the number summed vanishes if x^2-1 is a residue, is 2 if x^2-1 a non-residue, and is 1 in each of the two cases when $x^2-1 \equiv 0$. n expanding the right-hand side we get

$$N \equiv \{p+2+(-1)^{\frac{1}{2}(p-1)}\}/4$$
$$= I\,(p+3)/4,$$

here I means "greatest integer contained in," since each side is ss than p.

If N is the number of groups of quadratic residues containing ore than one of them, and $p = 4m+1$,

$$8N - 4Q2 \equiv \Sigma\,\{1-(x^2-1)^{2m}\}\,\{1+(x^2+1)^{2m}\},$$

$$8N - 4(-1)^m \equiv 1 + (-1)^m\,2\alpha,$$

hich gives $$N = \{p+1+2(-1)^m\,(2+\alpha)\}/8,$$

here α is defined as before, for the right-hand side is integral and ch side is less than p.

If $p = 4m + 3$ we have

$$8N - 2(1 + Q2) \equiv \Sigma \{1 - (x^2 - 1)^{2m+1}\} \{1 + (x^2 + 1)^{2m+1}\},$$

which gives $N = \{p - 1 - 2(-1)^m\}/8 = I(p+1)/8$.

It is obvious that the number of groups of quadratic non-residues is equal to the number of groups of residues if $p = 4m + 3$ and is one less if $p = 4m + 1$.

To find the number N of groups containing more than one non-residue we find the number of quadratic non-residues preceded by a non-residue and followed by a residue by evaluating

$$\Sigma \{1 - (x-1)^{\frac{1}{2}(p-1)}\} \{1 - x^{\frac{1}{2}(p-1)}\} \{1 + (x+1)^{\frac{1}{2}(p-1)}\},$$

and making allowance for the cases where

$$x - 1,\ x \text{ or } x + 1 \text{ are} \equiv 0,$$

and then deduce the value of N, remembering to add 1 if -1 and -2 are non-residues. The result is that if $p = 4m + 1$ then

$$N = \{p + 1 - 2(-1)^m \alpha\}/8,$$

and if $p = 4m + 3$ then

$$N = I(p+1)/8.$$

We can get the number of isolated non-residues by subtracting the number of groups found here from that found above.

If $p = 3m + 1$ and $4p = \alpha^2 + 3\beta^2$, where $\alpha \equiv 1$, $\beta \equiv 0$ mod. 3, then $\alpha \equiv -2m!/m!\,m!$ mod. p. If now N is the number of groups of cubic residues (including groups of one),

$$9(N-1) + 6 \equiv \Sigma \{2 - (x^3 + 1)^m - (x^3 + 1)^{2m}\}$$
$$\equiv 2 - \alpha,$$

whence $N = (2p + 5 - \alpha)/9$, for the right-hand side is integral and each side is less than p.

In the same way, but with more difficulty in the details, we can find the number of groups of bi-quadratic residues of a prime $p = 4m + 1 = \alpha^2 + \beta^2$, where $\alpha \equiv 1$ mod. 4, the result being

$$N = (3p + 7 + 6\alpha)/16$$

if m is even, and $N = (3p + 3 - 2\alpha)/16$ if m is odd.

16. If the number of groups of cubic residues is to be equal to the number of such residues we must have

$$(2p + 5 - \alpha)/9 = (p - 1)/3,$$

but $\alpha^2 < 4p$ whence $p < 16$, so that the only possible cases are 7 and 13, in which this does happen. Hence with these exceptions there is always some residue that is followed by a residue, and therefore the congruence $x^3 + 1 \equiv z^3$ can be solved with number

prime to the modulus for any prime modulus of the form $3m+1$ and hence for any modulus composed of such primes). Also from the number of groups we can find the number of residues followed by a residue, and hence the number of solutions of $x^3+1\equiv z^3$. The number of solutions of $x^3+y^3\equiv z^3$ is clearly $p-1$ times as great. The same* is true of the congruence $x^4+y^4\equiv z^4$, the excepted primes being 5, 13, 17, 41, and also of $x^2+y^2\equiv z^2$, the excepted primes being 2, 3, 5. We can also solve the congruence $x^2+y^2+1\equiv 0$ for any prime modulus except 2 or 5, for if p is of the form $4m+1$ we take x^2 to be congruent to any quadratic residue that is followed by a residue, and if p is of the form $4m+3$ we take x^2 to be congruent to any residue that is followed by a non-residue, e.g. the last residue of the group that begins with unity.

Taking the last result we see that every prime of the form $4m+3$ divides the sum of three squares that have no common divisor except unity.

Now by the process of § 12 we can prove† that any odd prime divisor of the sum of four (or three) squares that have no common divisor except unity is itself the sum of four squares at most. Hence every prime of the form $4m+3$ is the sum of four squares, and we know that every other prime is the sum of two squares, hence, using Euler's formula of composition, we see that every number is the sum of four squares at most.

The problem of the representation of a number N as the sum of three squares does not belong to our subject, but for the sake of completeness we sketch out a proof. If N is of the form $4m+1$ or $4m+2$, there are properly primitive forms of determinant $-N$ that have the quadratic characters of -1, and if N is of the form $8m+3$ there are improperly primitive forms of this determinant having the characters of -2, for in each case the genus in question satisfies the condition of existence, and therefore exists. Let such a form, transformed if necessary so that the first coefficient is prime to N, be (b, f, c), let $bg^2\equiv -1 \bmod. N$ be solved for g and let $a=(bg^2+1)/N$. Then

$$N=(a,\ b,\ c,\ f,\ g,\ 0)\,(bc-f^2,\ fg,\ -bg),$$

* We can always solve $x^n+y^n\equiv z^n \bmod. p$, where n is odd and p a prime of the form $3mn+1$, a solution being $x=1$, $y=g^m$, $z=-g^{2m}$, where g is a primitive root of p, and also in some other cases, e.g. if $n=5$, $p=131$ a solution is $x=1$, $y=23$, $z=16$. We can also solve the congruence to modulus n^2 if n is a prime of the form $4n+1$, the solution being as above, and also in some other cases, e.g. $n=59$, $x=1$, $y=3$, $z=4$, or $n=83$, $x=1$, $y=8$, $z=9$, but there is none for the other primes of the form $3m+2$ smaller than 100.

† We put $k=1$ throughout and prove that the new sum of four squares is less than the old sum unless this is even, and then is not greater than it and odd, and therefore less than it.

where $N = bc - f^2$, is a representation* of N in a definite ternary quadratic form of determinant 1. On reducing it in the ordinary way we have a representation of N as a sum of three squares at most.

If n is a prime and N the number of distinct solutions of the congruence $\phi(x) \equiv 0 \mod n$, we clearly have

$$N \equiv \Sigma [1 - \{\phi(x)\}^{n-1}]$$

subject to $0 < x < n$, but this method of finding the number of solutions in general gives formulae that are too complicated to be of any use.

* This is a particular case of the identity

$$(a, b, c, f, g, h)(Ax + Hy + Gz,\ Hx + By + Fz,\ Gx + Fy + Cz) = \Delta(A, B, C, F, G, H)(x, y, z).$$

The Mobility of the Positive Ion in Gases at Low Pressures. By GEORGE W. TODD, M.Sc., 1851 Exhibition Scholar, Emmanuel College, Cambridge. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 31 October 1910.]

The experiments of Rutherford*, Langevin†, Wellisch‡ and others on the mobility of gaseous ions show that for ordinary pressures the product of the pressure and mobility is constant. Below 20 cms. of mercury Langevin found in the case of the negative ions in air that this product increased rapidly with diminution of pressure, while with the positive ions there was only a tendency to increase. Langevin made observations down to 7·5 cms. Recently Kovarik§ has determined the mobilities of the negative ions in air and other gases down to pressures of 1 cm., and finds that the product of the pressure and mobility continues to increase very rapidly.

The experiments described in the present paper show that the velocity of the positive ion under unit electric force is inversely proportional to the pressure down to a few millimetres of mercury pressure.

A modification of Rutherford's alternating field method was used. The arrangement of the apparatus is shown in Fig. 1.

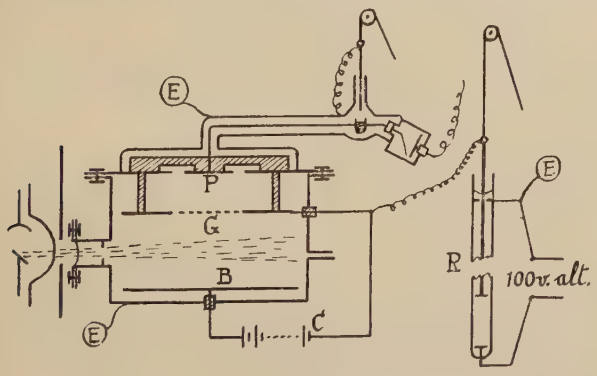


Fig. 1.

P is a carefully insulated metal plate connected to a tilted electroscope. 5 cms. below P is a gauze G which can be connected to a source of alternating potential of which the maximum may be

* *Camb. Phil. Soc. Proc.*, IX., 410.
‡ *Phil. Trans. Roy. Soc.*, A, 209, 249.
† *Annales de Chimie*, VII., 28, 1903.
§ *Phys. Rev.*, XXX., 4, 420.

altered as desired by means of the potentiometer arrangement at R. This is a copper sulphate resistance with its ends connected to the terminals of a 100 volt alternating circuit one of which is earthed. By moving a copper disc up and down in the solution varying alternating potentials were tapped off for the gauze G. The plate B being connected through the insulated battery C to the gauze G is always maintained at a constant higher potential than G, and therefore when the gas between them is ionised a stream of ions of one sign travels up to the gauze. The ionisation was produced by shining X-rays through an aluminium window in the side of the metal pot containing the plates.

Let u = velocity of ion per volt per cm.,

and d = distance between G and P.

Then velocity of ion at the instant G is at potential E is uE/d.

If $E = E_0 \sin 2\pi \dfrac{t}{T}$, where E_0 is the maximum potential and T is the period of alternation, the velocity at any instant is

$$\frac{uE_0 \sin \dfrac{2\pi t}{T}}{d}.$$

The electroscope will begin to show a deflection when the ions travel a distance d in time $T/2$. The condition for this is

$$d = \frac{uE_0}{d} \int_0^{\frac{T}{2}} \sin \frac{2\pi t}{T} \, . \, dt$$

$$= \frac{uE_0 T}{\pi d},$$

or

$$u = \frac{\pi d^2}{E_0 T}.$$

The voltmeter gives the "effective" value e of the potential. Hence if the instantaneous value E is $E_0 \sin pt$, then $E_0 = \sqrt{2}.e$. No correction was made for induction between the plates the correction amounting to less than 1 °/₀. The distance between the electroscope plate and the gauze was $d = 5{\cdot}0$ cms., and the number of alternations per second was 90, so that the mobility is given by

$$u = 5010/e.$$

In making a determination of the mobility the pressure was brought down to required dimensions by means of a mercury pump and read on a McLeod gauge. The electroscope was then insulated and the alternating potential switched on. If this potential was more than sufficient to make the ions getting through the gauze travel the distance d in $T/2$, the leaf would

slowly creep across the scale of the electroscope. With the maximum alternating potential less than a certain critical value there would be no charge communicated to the electroscope.

At the pressures used the ionisation was small, and as only a fraction of the ions formed get through the gauze the motion of the leaf was slow. An example of electroscope readings is given below and the curve obtained from them showing the critical point at P (Fig. 2). The first line in the table gives the effective voltage of the alternating field, the second gives the times taken by the electroscope leaf to travel across the same part of the scale, and the reciprocals of these which are proportional to the current to the leaf are contained in the third row.

Air : pressure = 6·10 mm.

Volts	60	53	46	39	34	22	42	66
Time	26·0	33·6	47·9	85·0	22·0	no motion	57·1	21·9
Current	385	297	208	118	45	—	175	455

Critical voltage = 29·2. ∴ Mobility = 173 cms./sec.

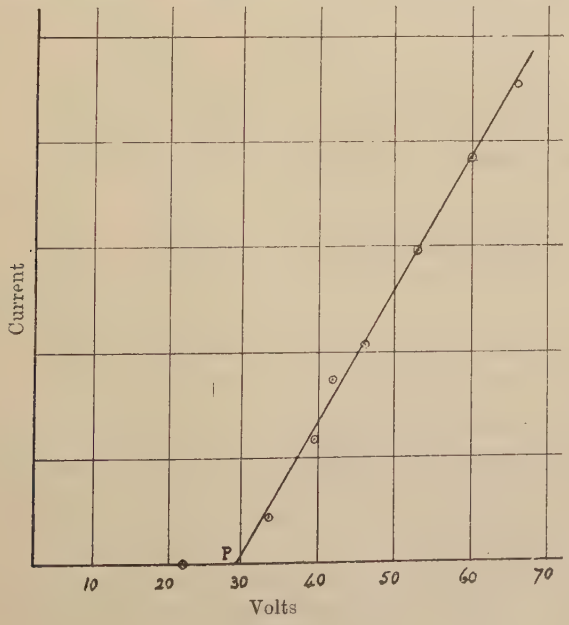


Fig. 2.

Experiments were made with four gases: air, carbon dioxide, hydrogen, and ethyl bromide vapour. The ionisation with hydrogen was so weak that readings could not be obtained below 4 mm. of mercury. The tables below give the results of the experiments.

Air

Pressure	Mobility	Product
mm.		
12·60	84	106
10·60	100	106
10·55	99	100
8·25	128	106
7·75	134	104
7·65	130	99
6·85	153	105
6·65	167	106
6·10	173	106
5·10	199	102
5·00	200	100
4·85	206	100
4·45	241	107
3·40	350	109

Carbon dioxide

Pressure	Mobility	Product
mm.		
8·70	83	72
8·40	85	72
7·25	105	76
6·85	108	74
5·40	132	72
4·62	164	76
3·74	212	79
3·12	241	75

Hydrogen

Pressure	Mobility	Product
mm.		
25·10	95	248
20·90	124	259
18·15	132	239
15·40	152	234
11·25	213	241
9·85	252	248
6·11	404	247
4·55	504	230

Ethyl bromide

Pressure	Mobility	Product
mm.		
5·12	82·2	42·2
4·40	96·1	42·3
3·70	113	41·9
2·40	177	42·5
1·62	266	43·1
1·34	307	41·1
·95	462	43·8

Observations of the mobility of the negative ions in air were made and the values obtained were of the same order as those obtained by Kovarik, showing an enormous increase in the mobility at low pressures.

Experiments show that the negative ion consists either of an aggregation of molecules about the charge, the aggregation becoming less complex at low pressures, or it consists of a single

molecule (or a constant number of them) with a corpuscle attached, the latter being able at low pressures to migrate from one molecule to another.

If the positive ion is an aggregation of molecules round a positive charge that aggregation persists down to the pressures used in these experiments. If there is a positive unit of electricity it is at ordinary temperatures and at pressures above two or three millimetres of mercury inseparable from the molecules forming the ion, otherwise an increase in mobility would have been the result. It may be that at high temperatures the positive unit does exist for a time in the free state for the mobility of positive ions in flames is much greater than that required by the temperature law.

The author is continuing the experiments with the ions given off when aluminium phosphate is heated, with the object of measuring mobilities at much lower pressures.

My thanks are due to Sir J. J. Thomson for his interest and encouragement during the experiments.

The Mobility of the Positive Flame Ion. By S. G. Lusby, M.A. (Sydney), Emmanuel College, Cambridge, Barker Graduate Scholar of the University of Sydney. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 31 October 1910.]

I. *Introduction.* The determination of the mobilities of the ions produced when salt vapours are introduced in flames has occupied the attention of many experimenters ever since Arrhenius* first set this type of work on an exact basis. Most observers, however, have confined their attention to the negative ion, probably owing to the rapid growth of our knowledge of the negative electron. It has now been demonstrated beyond all doubt by Gold† and H. A. Wilson‡ that in high temperature flames the negative ion is a pure electron. Within the last few years, however, the attention of physicists has been transferred to the positive ion, chiefly on account of the problems suggested by Kanalstrahlen, and the conception of a positive electron—not necessarily of similar mass, but of similar charge to that of the negative electron—has steadily gained ground. The present experiments have been carried out with the object of determining the velocity of the positive flame ion under unit conditions, and it has been deduced from the results obtained that the positive ion at a temperature of 1500° absolute has a mass very closely equal to that of the hydrogen atom, i.e. a mass identical with that of the "secondary" particles in the Kanalstrahlen.

The first determination of the velocities of flame ions was made by H. A. Wilson§. His results may be briefly summarised thus:—at 2000° absolute, for salts of alkaline and alkali earth metals, the positive velocity is 62, the negative velocity 1030 centimetres a second—both under a gradient of one volt per centimetre; in hot air at 1000° abs., alkaline salts gave 7·2, alkali earth salts 3·8 for the positive ions, both groups of metals giving 26 for the negative ions. It is now known that these results are inaccurate owing to errors introduced in the calculation of the potential gradient between the electrodes. In the negative measurements, a uniform gradient was assumed, whilst in the positive measurements, the gradient was plotted, but only for a pure flame, whereas the salt bead introduced in the experiments very appreciably influences the distribution. Nor can one infer

* Arrhenius, *Wied. Ann.*, 1891.
† Gold, *Proc. Roy. Soc.*, 79, A, 1907.
‡ Wilson, *Proc. Roy. Soc.*, 82, A, 1909.
§ Wilson, *Phil. Trans.*, A, 1899.

that these results are relatively true, for the shape of the potential curve depends on which electrode is uppermost. The correct value for the mobility of the negative ion has been since determined by Gold [*loc. cit.*] and Wilson [*loc. cit.*], and both agree that it corresponds to that of an electron. Marx*, from consideration of the fall of potential in the flame, has also deduced the ionic mobilities. His method, however, was very indirect and is based on a doubtful assumption, viz., that the ionisation is uniform throughout the flame, and negligible at the upper electrode. His results for the positive ion varied from 120 to 340, with a doubtful mean of 250. The only other measurements which concern us are those of Moreau†, who deduced 80 cm. a second for the velocity at 2000° abs. Moreau's results are also vitiated by the assumption of a uniform potential gradient in the flame.

II. *Experimental Details.* The method adopted in the present series of measurements was that employed by Wilson in 1899. In this method two electrodes are placed horizontally above one another in the flame, and the current between them is measured for different potential differences, the upper plate being charged positively. A small bead of salt is then introduced into the flame just below the upper electrode, and the current measurements are repeated. When the potential difference is great enough to drive back the positive ions against the uprush of the gas, the current suddenly increases. The exact potential difference required is got by comparing the two current curves. Knowing this critical voltage, the upward velocity of the gas, and the *minimum* potential gradient in the flame, one can easily deduce the mobility. The experimental arrangements were a modification of those used by Wilson. The electrodes were brass discs 14 cm. in diameter with circular pieces 5 cm. in diameter cut out of their centres. In the case of the lower electrode, platinum wires were strung across the centre of the disc to form a mesh about 3 mm. wide; to the upper disc was clamped a piece of platinum gauze. Each electrode was supported by three glass rods inserted in a base board; those for the upper one were set at a permanent height, whilst the others could slide through holes cut in the board and thus be fixed at any desired height. Large holes were drilled in the lower disc through which these latter rods might pass without contact. The base board was suitably supported on insulating legs. The burner employed was a plain brass tube of internal diameter 0·68 cm., passing through a larger tube in which it was fixed at the lower end by a cork and at the

* Marx, *Ann. der Phys.*, II., 1900, p. 790.
† Moreau, *Ann. de Chim. et Phys.*, 1903.

upper end by three centring screws. The outer tube passed through the centre of the base board and could be set at any required height. The air and gas supplied to the burner were previously mixed in a small jar and their pressures measured by means of water gauges just as they entered the mixing jar. The air was supplied from two large gasometers which gave a very constant stream whose volume was accurately known. The gas was drawn from the laboratory mains and passed through two large carboys in succession and then through a micrometer tap before entering the mixing vessel. This arrangement was found to successfully damp out any fluctuations in pressure, and by slightly turning the micrometer head, any permanent variation could be counteracted, though this was not often necessary. The constancy of the flame was fixed by two conditions—the height of the inner blue cone, and the air pressure. A kathetometer which could be trained on to either the flame or the water gauge ensured constancy in these two factors. Under these circumstances, the blue cone as seen with the naked eye was very steady and exhibited only very slight fluctuations when viewed through the kathetometer telescope. The dimensions of the flame used were:—inner cone 1·5 cm., outer cone 7·0 cm. The electrodes were placed 3 cm. apart, and were connected through a battery of small cells to a galvanometer whose sensitiveness was 10^{-8} ampères per scale division. In order to prevent conduction of ions down the side of the flame, a piece of gauze with a circular hole in the centre was placed just above the lower electrode and joined direct to the negative pole of the battery, but not through the galvanometer. The salt bead used was about 2 mm. in diameter, and the platinum wire holding it was fused into a glass rod which could be swung in and out of the flame so as always to occupy the same position.

III. *Account of Observations.* A search was made to see if the critical voltage depended at all on the salt used, and also to find out whether the alkaline earth salts gave a characteristic velocity at this particular temperature—1500° abs. First of all a careful test of the constancy of the ions from various salts of a given metal was made. Potassium was chosen because its salts are cheap and easily procurable, whilst its conductivity is high. The following salts were tried:—

K_2CO_3; KOH; KCl; KBr; KI.....Simple Salts.
$K_2Mn_2O_8$; $KNaCO_3$; $K_2Fe(CN)_6$.....Complex Salts.

In no case were the variations of critical voltage outside the limits of error; it was hoped that the complex salts might exhibit some singularity, but none resulted. It is interesting to note that the permanganate is an ideal salt for measurement; its con-

ductivity is fairly high, its volatility very small, so that a bead lasts an indefinite time, whilst the inevitable change that must occur in its chemical composition, does not seem to affect its ions.

The nitrate was also tried, but as it exhibited a tendency to splutter on the electrodes, and was extremely volatile, it was abandoned. An examination of the various salts of the other conducting metals was then made, the following being tried:—

Na_2CO_3;	NaOH ;	NaCl
LiBr;	(Li_2SO_4)	
RbCl;	Rb_2CO_3	
CsCl;	Cs_2CO_3	

} Monovalent Metals.

$BaCO_3$;	$BaCl_2$
$SrCO_3$;	$SrCl_2$
$CaCl_2$;	$(CaCO_3)$

} Divalent Metals.

It was found that all these salts gave identical results. It was difficult to get reliable results for lithium. The bromide alone could be depended on; the sulphate was also tried, but nothing reliable can be deduced from it. Calcium also presented difficulties. The chloride was the only salt whose conductivity was high enough, and it had to be well dried immediately before the experiment. None of the other salts call for special mention. The difficulties were mainly those of volatility; if this be too low, the current is feeble, whilst if it be too high, the vapours tend to condense on the upper electrode and permanently increase the current. Ammonium salts were tried as members of the potassium group, but proved altogether too volatile to work with. The mean value of the critical potential difference deduced from 35 of the best curves was 62 volts. A typical curve is shown in Fig. 1, where ordinates represent current and abscissae the potential difference between the electrodes.

IV. *Determination of the Potential Gradient.* In order to determine the fall of potential, a fine platinum wire fused into a glass rod was introduced into the flame. The rod was supported on the travelling frame of a vertical micrometer thread. The potential taken up by the wire was measured by a quadrant electrometer whose needle with one pair of quadrants was joined to an electrode, whilst the other pair was connected to the search wire. The search wire was moved in steps of 2 mm., and, where the gradient was small, of 1 mm. After taking readings with the upper electrode joined to the electrometer, the lower one was in turn joined up and the readings repeated. This counteracted the error due to small readings near the electrode. The potential

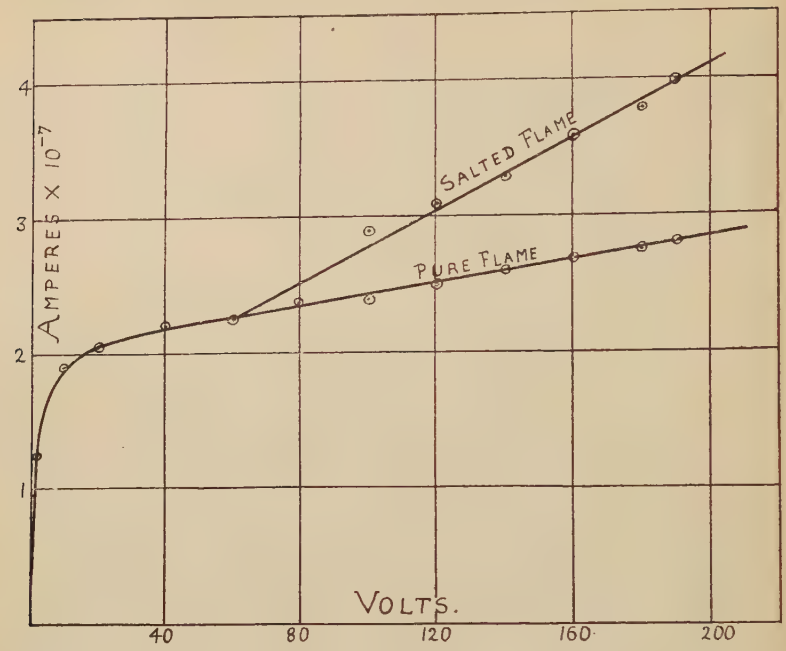

AMPERES X 10^{-7}
4
3
2
1
SALTED FLAME
PURE FLAME
VOLTS.
40
80
120
160
200

Fig. 1.

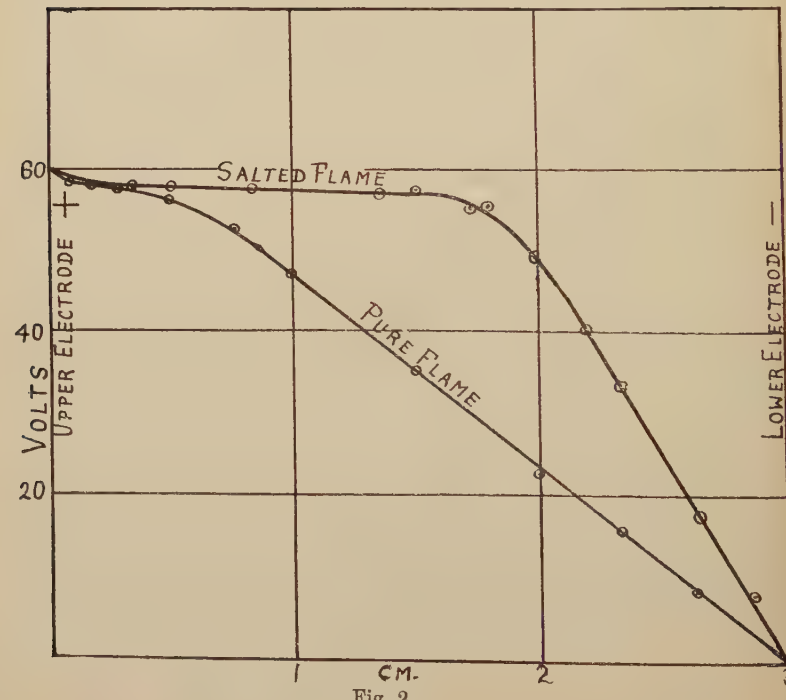

60
40
20
VOLTS
UPPER ELECTRODE +
LOWER ELECTRODE —
SALTED FLAME
PURE FLAME
1
CM.
2

Fig. 2.

difference applied was that found in § III. above, viz. 62 volts. In order to determine the error introduced by plotting the current in the pure flame, a set of readings was first taken under these conditions. A bead of potassium carbonate was then introduced and the readings repeated. Specimen curves are shown in Fig. 2. By comparing the two results it was found that in the former case the minimum gradient is over nine times as large as in the latter. The mean results obtained were:—for the pure flame 6·51 volts per cm., for the salted flame 0·71 volts per cm. In general, the incandescent search wire takes up a potential even when the electrodes are joined together. This effect, it was found, was quite negligible in comparison with 60 volts.

V. *Velocity of the Gas.* The determination of the upward velocity of the flame gases was made from a comparison of the pressures of the air and the gas, and the volume of air used. For this purpose a water gauge was used to measure the pressure of the gas immediately before entering the burner. The gas was first turned on, and the pressure read through the kathetometer telescope; the air was then turned on, and the pressure again read. The exact volume of air used was determined from the rate of fall of the reservoir. The mean results obtained were as follows:—

$$\frac{\text{air pressure}}{\text{gas pressure}} = 9{\cdot}4,$$

$$\text{volume of air per second} = 68{\cdot}3 \text{ c.c.},$$

$$\text{therefore} \qquad \text{volume of gas per second} = 7{\cdot}27 \text{ c.c.}$$

Total volume of mixed gases = 75·57 c.c. per second.

As the diameter of the burner was 0·68 cm., the velocity of the mixed gas works out at 206 cm. per second. This calculation neglects the outward expansion of the gas, but the order of accuracy obtained is quite as high as in the other portions of the experiment.

VI. *Final Result.* The mobility is determined from the simple relation $V = kX$. We have found that

$$V = 206 \text{ cm. per second}; \quad X = 0{\cdot}71 \text{ volts per cm.}$$

Hence the mobility (k) = 290 cm. per second.

VII. *Temperature.* The temperature of the flame was measured by means of a thermocouple whose members were Platinum and a 10 per cent. Rhodium—Platinum alloy. The couple was standardised by the melting of beads of potassium carbonate and potassium sulphate. Its indications were found to agree fairly closely with those of a similar couple investigated in

detail by Sosman*. The temperature fell off somewhat in the upper part of the flame; the value adopted as corresponding to the mobility given, was the mean temperature for that part of the flame in which the minimum potential gradient was observed, viz. 1450° absolute. An attempt was made to use the couple as a potential explorer, but it was given up as its members tended to distort themselves when heated.

VIII. *Theoretical Considerations.* Knowing the mobility of the ion, one can calculate its mass from the relation $k = \lambda e/mv$, where the various quantities have their usual meanings. This formula assumes that the ion comes to rest at impact, but otherwise seems to be quite legitimate and should give accurate results provided we correctly interpret λ and v. The free path of a particle of mass m_1 moving in a gas whose molecular mass is m_2 is given by

$$\lambda_1^{-1} = \pi n_2 \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \cdot \sqrt{1 + \frac{m_1}{m_2}},$$

where

σ_1 = diameter of the ion,

σ_2 = diameter of the molecule,

n_2 = no. of molecules per c.c.

Putting $m_1/m_2 = x$ and $\sigma_1/\sigma_2 = y$, this becomes

$$\lambda_1^{-1} = \lambda_2^{-1} \cdot \left(\frac{1+y}{2}\right)^2 \cdot \sqrt{\frac{1+x}{2}},$$

where λ_2 is the free path of a molecule of the gas. The velocity of the ion is given by

$$m_1 v_1^2 = m_2 v_2^2,$$

whence we get finally as the mobility of the ion

$$k_1 = \frac{\lambda_2 e}{m_2 v_2} \cdot \left(\frac{2}{1+y}\right)^2 \cdot \sqrt{\frac{2}{x(1+x)}}.$$

In this equation, everything but x and y is known, and if we knew the exact relation between x and y we could calculate the mass of the ion from its mobility. Unfortunately the connection between the mass and the diameter of a molecule is very complex. To assume that the mass varies as the diameter cubed or squared, as is frequently done, must lead to very inaccurate results. For example, the radius of a hydrogen molecule is $1{\cdot}01 \times 10^{-8}$ cm., that of an oxygen molecule $1{\cdot}41 \times 10^{-8}$ cm., and in this case, the mass varies as the ninth power of the radius. In view of this difficulty,

* Sosman, *Amer. Journ. Sci.*, July, 1910.

the solution will be made in the inverse direction, i.e. we shall calculate the mobility of an ion of given mass. A rough calculation leads one to suppose the ion is of about the same mass as a hydrogen atom; we shall therefore calculate the mobility of an ion of such a mass at the temperature of the experiment, i.e. 1450° abs. The following quantities enter into the calculation :—

$$\left.\begin{aligned}\lambda_2 &= 51 \times 10^{-6} \text{ cm.} \\ v_2 &= 104 \times 10^3 \text{ cm./sec.}\end{aligned}\right\} \text{ at } 1450°,$$

$$\frac{e}{m_2} = \frac{3 \times 10^{14}}{29} \text{ E.S.}$$

$$x = \frac{1}{29},$$

$$y = \frac{0{\cdot}50}{1{\cdot}41},$$

whence $k = 276$ cm. a second under a gradient of 1 volt per cm. Applying the same formula to an electron, for which

$$x = \frac{1}{29 \times 1700},$$

$$y = 10^{-5} \text{ and is negligible,}$$

we find $k = 22{,}000$ cm. per second. Now the present experiments gave the positive flame ion a mobility of 290, which is very close to that calculated for a hydrogen atom. Also the experiments of Gold (*loc. cit.*) gave 13,000 as the mobility of the negative flame ion which is known to be an electron. The agreement in this case is fair, considering the uncertainty of the quantities involved. The above calculation seems to suggest very strongly that the positive flame ion either is, or else has the same mass as, a hydrogen atom. It will be observed that if the formula proposed above be true, then the mobility should vary as the square root of the absolute temperature. Experiments are now in progress to test this law, and also to find out at what temperature the "cluster-ion" of ordinary temperatures becomes reduced to a single body as small as a hydrogen atom; or, in other words, to determine at what temperature differentiation in ionic mobility ceases. In view of a continuation of the present work in order to test the theory proposed, it would be futile to discuss at this stage of the work the questions raised by the identity of the positive flame ion with the hydrogen atom, and its relations with Kanal particles and "thermions."

IX. *Summary.* (i) The velocity of the positive ions produced by introducing a salt bead into a Bunsen flame has been measured by H. A. Wilson's method.

(ii) For metals of the alkali and alkaline-earth groups, the velocity is 290 cm. a second in practical units, at a temperature of 1450° abs.

(iii) This velocity is independent of the particular salt of the metal used, whether simple or complex.

(iv) From a theoretical formula proposed, it has been deduced that at the temperature of the experiments, the positive ion has a mass very nearly equal to that of a hydrogen atom.

In conclusion, I desire to thank Professor Sir J. J. Thomson for helpful suggestions made during the course of these experiments.

Note on the Fundamental Theorem of Integration. By W. H. Young, Sc.D., F.R.S., sometime Fellow of Peterhouse.

[*Received in revised form* 24 November 1910. *Read* 28 November 1910.]

§ 1. In a paper published in the *Quarterly Journal** it is shown that all of Lebesgue's celebrated theorems may be proved without the use of Cantor's numbers, or Cantor induction, provided only we assume that one of them which asserts that one may proceed by integration from a derivate to its primitive function, whenever that derivate, or one of the derivates, is finite, except at most at a reducible set of points. Further, in a joint paper by my wife and myself on the existence of a differential coefficient†, it is shown that the particular case of this theorem in which the derivate in question, and therefore every one of the derivates, is bounded may also be proved without Cantor's numbers. From the mode of reasoning adopted in the former of these two papers, which employs, in fact, only the special case, and not the more general theorem, it follows that all Lebesgue's results, with the exception of the following, may now be asserted to be true independently of Cantor's numbers, or Cantor induction:

(i) The necessary and sufficient condition in order that the indefinite integral of a derivate which is not bounded, and which is infinite at most at a reducible set of points, should be the primitive function of the derivate is that the derivate should be summable;

(ii) The necessary and sufficient condition that the indefinite integral of a derivate which is not bounded, and which is infinite at most at a reducible set of points, should be the primitive function of the derivate is that the primitive function should be of bounded variation.

The second of these theorems follows from the first by means of the theorem that the derivates of a function of bounded variation are necessarily summable, a theorem which is one of those proved without the use of Cantor's numbers. It remains, therefore, only to prove the first of the two theorems without using Cantor's numbers, or Cantor induction.

I have not yet succeeded in obtaining such a proof. On the other hand, I have been able to prove, without these means, a theorem which like (i) includes (ii) as a particular case, namely:

The necessary and sufficient condition that the indefinite integral

* W. H. Young, "On Functions of Bounded Variation" (1910), *Quart. J.*, pp. 54—85.

† Presented to the London Mathematical Society.

of a derivate which is not bounded, and which is infinite at most at a countable set of points, should be the primitive function of the derivate is that the primitive function should be of bounded variation.

I propose in the present note to communicate my proof of this result to the Society.

§ 2. That the condition in the theorem to be proved is necessary is, of course, obvious, as a Lebesgue integral is always a function of bounded variation. We have therefore only to prove that the condition is sufficient.

Let then

$$y = f(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

be a function of bounded variation. Then, by one of the theorems above referred to*, the derivates of $f(x)$ are necessarily summable. Moreover they agree, except for a set of values of x of content zero. Further, by the property of a function of bounded variation, the curve (1), using the word curve in the usual generalised sense, has, by a known theorem†, an arc. The abscissa x is necessarily, since y is a one-valued function of x, a monotone function of the arc s, say a monotone increasing function. Hence $\frac{dx}{ds}$ exists, except for a set of values of s of content zero. Further, y is a one-valued function of s, and its derivates with respect to s, like those of x, necessarily lie numerically between 0 and 1. Hence, by the particular case of Lebesgue's theorem (i), which has been proved without the use of Cantor's numbers, $\frac{dy}{ds}$ exists, except for a set of values of s of content zero, and has y for its integral with respect to s. For the same reason x is the integral of $\frac{dx}{ds}$ with respect to s, the integral being, of course, taken in each case over the set of points at which the integrand exists. Hence

$$f\{x(s)\} = y(s)$$

is, when regarded as a function of s, an integral.

Now x is a monotone increasing function of s, and $\frac{dx}{ds}$ and $\frac{dy}{ds}$ are never zero together, since the sum of their squares is unity.

Take a value of s not belonging to the exceptional set of zero content. As we make s approach the value in question, x will alter continuously, and will move up to the corresponding

* "On Functions of Bounded Variation," § 23, p. 81.

† See *Theory of Sets of Points*, Camb. Univ. Press, 1906, pp. 266 sq.

value of x; there is, in fact, a one-one-correspondence between x and s. Consider then the equation

$$\frac{y(s+k)-y(s)}{k}=\frac{f(x+h)-f(x)}{h}\cdot\frac{x(s+k)-x(s)}{k},$$

where we have written

$$x(s+k)=x+h.$$

We remark that the left-hand side, and the second factor of the right-hand side, necessarily have as k approaches zero unique limits, which are not both zero. If neither is zero, the first factor on the right-hand side will have an unique finite limit. If the second factor on the right has zero as unique limit, the first factor on the right has infinity as unique limit, with determinate sign. Thus we have shown that $f(x)$ has, except for a set of values of x corresponding to a set of values of s of zero content, a differential coefficient $f'(x)$, which is either finite or infinite with determinate sign*.

Now suppose for definiteness it is the lower right-hand derivate of $f(x)$ which is known to be finite except for a countable set of values of x. Then, since there is one-one-correspondence between the variables x and s, it follows that this derivate is finite except for values of x corresponding to a countable set of values of s.

Hence the upper right-hand derivate of $f(x)$ cannot be infinite except for values of x corresponding to a set of values of s of zero content. Thus $f'\{x(s)\}$ exists and is finite, except for a set of values of s of zero content.

Hence, except at a set of values of s of content zero, we have the equality

$$y'(s)=f'\{x(s)\}\,x'(s),$$

each of the expressions $y'(s)$, $f'\{x(s)\}$ and $x'(s)$ being finite.

Integrating, then, we have

$$\int y'(s)\,ds=\int f'\{x(s)\}\,x'(s)\,ds.$$

Now $y(s)$ is an integral, and accordingly the integral of its differential coefficient, the integral being taken over the set of points at which that differential coefficient exists and is finite. Hence, to a constant *près*,

$$y(s)=f(x)=\int f'\{x(s)\}\,x'(s)\,ds.$$

But, by the theory of integration by substitution†, since $f'(x)$

* That it possesses a differential coefficient except for a set of values of x of zero content was known *a priori*, since it is a function of bounded variation.

† For a proof of the theorem here used see H. Lebesgue, "Sur les intégrales singulières" (1910), *Ann. de Toulouse*, p. 44.

Reference may also be made to a paper by the author in the *Proceedings of the London Mathematical Society* (1910), entitled "On a New Method in the Theory of Integration."

A special case of the general theorem is given by Hobson, *Proc. L. M. S.*, Series 2, Vol. VIII., p. 17 (1909).

is summable, since x is an integral and a monotone increasing function of s and since $f'\{x(s)\}$ is finite except for a set of values of s of content zero, we have

$$\int f'(x)\,dx = \int f'\{x(s)\}\,x'(s)\,ds.$$

Hence, finally, to a constant *près*,

$$f(x) = \int f'(x)\,dx.$$

Thus the theorem has been proved.

§ 3. If with Bernstein* we admit the existence of sets which, without being countable, none the less have no perfect component, the statement in § 2 is not the most general which can be made. The correspondence between x and s is not only a one-one-correspondence, but a continuous one-one-correspondence, therefore a set of the type in question of values of s or x corresponds to a set of the same type of values of x or s. Moreover the content of such sets is necessarily zero. Now the fact that the countability of the set is invariant for one-one-transformation, and that a countable set has zero content, are the only properties of the countable set of exceptional points in the above theorem that have been used in the proof; consequently we may say that the necessary and sufficient condition that the indefinite integral of a derivate which is not bounded, and which is infinite at most at a set of points having no perfect component, should be the primitive function of the derivate, is that the primitive function should be of bounded variation.

Bearing in mind, however, that examples have been constructed† of functions of bounded variation which are not the integrals of their derivates, and which possess at a perfect set of points no finite derivate, we see that our theorem may be further transformed as follows:

The necessary and sufficient condition that it should be possible to assert from a knowledge of the distribution of the infinities of its derivates alone that a function of bounded variation should be an integral (and therefore the integral of its derivates) is that one at least of its derivates should be finite at some point of every perfect set.

* F. Bernstein, "Zur Theorie der trigonometrischen Reihen" (1908), *Leipz. Ber.* pp. 325—338.

† H. Hahn, *Monatschr. für Mathematik* (1905), Vol. XVI. p. 161.

Nuclear relations of Paramecium caudatum during the asexual period. (Preliminary Communication.) By K. R. Lewin, B.A., Trinity College. (Communicated by Mr A. E. Shipley.)

[*Read* 14 November 1910.]

It is possible to divide a living Paramecium so that each merozoite, or fragment, receives a portion of the meganucleus. Owing to its small size, the solitary micronucleus of this form escapes section, and passes entire to one merozoite.

Except when an individual already preparing for fission was operated on, it was found that only one merozoite (at the most) recovered the normal body form and proceeded to divide.

The presence of the micronucleus is not the factor which decides whether a merozoite can divide, for in a few cases the surviving fragment gave rise to a culture of Paramecia without micronuclei.

The fact that the greater number of survivors in these experiments proved to contain a micronucleus is accounted for by the larger fragment (which most frequently survived) being more likely to contain the micronucleus of the original form; there is no proof that the presence of this organella contributes in any way to the viability of the merozoite.

The "Amicronucleate" Paramecia were capable of propagating by normal fission over considerable periods; one merozoite obtained by section on June 1st, 1910, gave rise to a culture which persisted until July 24th.

The animals appeared quite normal and, except for the absence of a micronucleus, divided in the usual way.

Their multiplication was not very vigorous, but then cultures arising from a "typical" Paramecium often shew an equal lack of reproductive vigour. However, as subsidiary cultures started at 23° C. (the main culture being kept at room temperature—about 17°) rapidly died out, it is very possible that the absence of the micronucleus may render the animal more delicate in constitution.

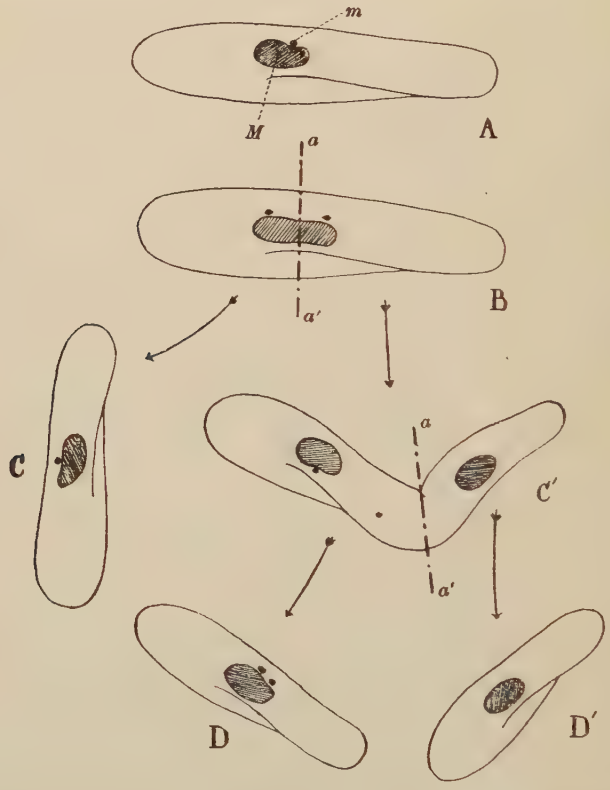
The production of a race of Paramecia without visible micronuclei cannot be explained by supposing that the micronucleus has fused with the meganucleus under the influence of the operation, for in one experiment, a stained preparation of one merozoite shewed it to possess the micronucleus, whilst the other fragment gave rise to a race provided with meganucleus only.

When an individual in division was cut, both merozoites were capable of further division. One case of section during the earliest stages of division led to an interesting result.

The animal shewed no outward sign of division, but must have possessed already two micronuclei.

One of the merozoites regenerated the typical shape, and gave rise to a culture of normal Paramecia.

The other made an abortive attempt to divide, and produced the monstrous form shewn in text-fig. 1 *C′*.



Text-figure 1. Diagram of origin of three types of *Paramecium caudatum*.

A. Normal non-dividing Paramecium.
B. Early division stage. *a*...*a′* plane of section.
C. Animal from culture arising from one merozoite. Nuclear relations normal.
C′. Monster formed by incomplete division of the other merozoite. The division was completed by a cut in plane *a*...*a′*.
D. Type with two micronuclei.
D′. Type without micronucleus.

M = meganucleus. *m* = micronucleus.

The meganucleus was seen in life to be divided. This fission was completed artificially, and the products isolated. Both divided, producing respectively an "amicronucleate" race and one with two micronuclei per individual. (See text-fig. 1.)

It was noticed that the "amicronucleate" culture shewed a lower division-rate than the others. No conclusion can be drawn from this as to the effect of the micronucleus upon reproduction, as the parent individual (*D'* in text-figure) contained a normal-sized nucleus in a comparatively small body, and may well have been thrown at the outset into a condition of depression by this disproportion. On the other hand it is quite possible that the micronucleus does exert an influence on the rate of division.

These experiments shew, as regards *Paramecium caudatum* at least, that the statement of Le Dantec* concerning the regeneration of the micronucleus from the meganucleus after merotomy, is incorrect.

They also demonstrate that the interaction of cytoplasm and meganucleus is sufficient to maintain the discontinuous growth of the cell during a considerable period.

Since under normal circumstances no two sister-merozoites were found to divide, there is a suggestion that possibly there exists in the cell a localised division-centre, which passes on section to one merozoite, leaving the other incapable of division.

At present this remains as a possibility, but when further evidence is obtained I hope to deal more fully with the matter in a subsequent paper.

* Le Dantec, "La Régénération du micronucleus chez quelques Infusoires ciliés," *C. R. Acad. Sci. Paris*, cxxv.

The feeding value of mangels. By T. B. Wood, M.A., Gonville and Caius College, Drapers Professor of Agriculture.

[*Read* 14 November 1910.]

This paper is a sequel to a communication on the chemical composition of mangels read to the Society in 1905. In this communication it was shown that the hundred or more varieties of mangels commonly grown by farmers can be reduced to five types as follows:

Name of type	Description	Average content of dry matter %	Yield of roots per acre. Tons	Yield of dry matter per acre. Tons
White fleshed globe	globe shape, white flesh	10·7	29·9	3·2
Intermediate	oval shape, cream coloured flesh	12·0	27·4	3·3
Golden Tankard	short cylindrical shape yellow flesh	13·1	24·6	3·2
Golden Globe	globe shape, yellow flesh	13·4	25·0	3·3
Long Red	long cylindrical shape, pink flesh	13·1	29·9	3·9

These figures show that the Long Red type grows much more food per acre than any other type.

The investigation described below was undertaken by Professor Middleton with the object of ascertaining if the feeding value of the various types of mangels was in practice proportional to their content of dry matter. This is by no means a simple matter for the ratio of the dry matter in the extreme case of white fleshed globe and long red is only 10·7 : 13·1, i.e. 100 : 121. But mangels cannot form more than about half the dry matter of the diet of animals, so the actual difference to be measured amounts to only about 10 per cent.

Mr A. B. Bruce, M.A., of Peterhouse, has kindly worked through the published data of many feeding trials dealing with about 400 animals, and finds that the probable error of one animal amounts to 14 per cent. of the average increase in weight during the feeding period.

From this it follows that it is necessary to make comparative tests with at least 25 animals getting each ration in order to be able to get a really significant result. It was impossible to deal with numbers of this size on the University Farm, but the necessary precision was obtained by repeating the trials, not only at Impington but at the home farms of Messrs E. R. Pratt of Ryston Hall, Norfolk, and H. Shepherd Cross of Hamels Park, Herts, to whom the writer is greatly indebted.

As the result of a series of seven trials in which two lots of animals were fed side by side on rations containing equal amounts of cotton or linseed cake and chaff, but differing in that one lot received white fleshed globe mangels and the other an equal quantity of Long Reds, it was found that the increases of live weight were in the proportion of $100 : 116 \pm 4$ in favour of Long Red. During the series of experiments 90 animals were used, 45 for each ration. By this means the probable error was brought inside the difference which was under measurement.

It will be noticed that the difference found is four times the probable error of the experiment, and it is therefore fair to conclude that there is a real difference in feeding value in favour of Long Red, most probably at least 10 per cent.

Two more trials were made, in which the varieties of mangels compared were Golden Tankard and Long Red. These varieties contain equal percentages of dry matter and should give identical results in feeding. On the two occasions when they were compared, the differences in live weight observed were well inside the probable error.

The result of the two sets of trials is to make it practically certain that the percentage of dry matter in mangels may be taken as an index of their feeding value.

Note on the spermatogenesis of Abraxas grossulariata (currant moth). By L. Doncaster, M.A., King's College.

[*Read* 28 November 1910]

I have already shown * that in this moth the *grossulariata* character is a Mendelian dominant, and further is not borne by eggs which contain the female determiner. It seemed therefore that a study of the cytology in this species might throw light on the possible relation between a chromosome and a Mendelian character. The spermatogenesis has therefore been investigated in both the parent forms (*grossulariata* and *lacticolor*) and in the heterozygote.

The spermatogonial mitoses are very small, and I have not been able to make any accurate counts of chromosomes, but the number is between 50 and 60. In different follicles two kinds of primary spermatocytes are found, one of which, though usually less frequent, may be regarded as normal, the other abnormal. The normal type will be described first. After the growth-phase, the first spermatocyte division consists of a spindle with very regular equatorial plate, containing 28 chromosomes of nearly similar size. These become dumb-bell shaped, divide, and pass in a regular anaphase to the poles. The second division is similar except in its smaller size; 28 chromosomes appear and all divide regularly. The spermatids so formed seem to develop into normal spermatozoa. No difference is found between testes of pure *grossulariata*, *lacticolor*, and heterozygotes. The second type of spermatocytes is relatively more abundant in older testes; the cells and nuclei are smaller, and in division the equatorial plates are strikingly different from those of the first type in their irregularity, which makes accurate counting impossible. The chromosome number is approximately 28. The anaphases are even more irregular, the chromosomes often being scattered all over the spindle, but eventually all reach the poles and form the nuclei of the secondary spermatocytes. These divide by a similarly irregular mitosis, and form spermatids smaller than those of the first type. As these become converted into spermatozoa the nucleus travels along the tail, and seems finally

* *Reports to Evolution Committee, Royal Society*, iv., p. 53.

to degenerate, as was described by Meves* in the "apyrene" spermatozoa of the moth *Pygaera*, but I have not observed the final stages of degeneration.

From the fact that the same process occurs in both varieties, and that usually the expected sexual and Mendelian ratios are found in breeding experiments, it is to be concluded that two types of spermatozoa are not correlated with different heritable characters, and probably those of the second type are not functional in fertilisation.

Oogonial mitoses do not differ recognisably from those of the spermatogonia.

* *Arch. Mikr. Anat.*, LXI. (1903), p. 62.

The Ionisation of Heavy Gases by X-rays. By R. T. Beatty, M.A., B.E., Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 31 October 1910.]

When certain heavy gases, such as $Ni(CO)_4$, AsH_3, SeH_2, are ionised by X-rays, the ionisation produced (considered relatively to that produced in air at the same pressure) remains constant for any particular gas till the X-rays attain to a certain penetrating power. When this stage is reached the relative ionisation increases to several times its original value and remains in the neighbourhood of this abnormal value while the penetrating power of the X-rays continues to increase. What is the cause of this sudden increase? Some light may be thrown on the effect by observing that the substance ionised shows an abnormally great absorption of the X-rays just at the point where abnormal values of the ionisation are observed, and in fact now begins to emit a characteristic X-radiation and an increased quantity of β-rays.

Probably then the increased ionisation may be due to these causes.

An attempt was accordingly made to detect the emission of β-rays from the gas SeH_2 when ionised by X-rays penetrating enough to evoke the characteristic X-radiation of Se. The gas was admitted to a shallow ionisation chamber at different pressures, and a curve plotted connecting ionisation with pressure. If some of the ionisation were due to β-rays from the gas the curve should at low pressures be convex to the axis of pressure. This effect was strongly marked in all cases where the X-rays were sufficiently penetrating.

If now the chamber be lined with a film of Se, the curve should become a straight line through the origin, since the film may be considered from the point of view of a β-ray generated in it as forming an infinitely thick envelope of Se in a gaseous state round the ionisation chamber, so that any β-rays which are generated in the gas in the chamber and strike the walls before using up all their energy in ionisation, are balanced exactly by β-rays coming from the film. This linear curve was found to represent the experimental results.

Curves were also drawn connecting ionisation with pressure when air was used in the chamber lined with Se. These curves give sufficient data to calculate how much ionisation is produced by

1°. Direct formation of δ-rays by the X-rays.

2°. Formation of β-rays by the X-rays.

As sources of radiation a number of elements, whose atomic weights lie between that of Fe and that of I, were used. These elements can be made to emit characteristic X-radiations.

When the radiations from Fe, Ni, Cu, Zn, Se were used the relative ionisation of SeH_2 was found to be equal to 30 ± 5.

When Sr, Mo, Ag, Sn, I, were used the relative ionisation increased greatly, attaining a value of 286 with the radiation from I. A large part of the ionisation was found to be due to the β-rays, emitted by the gas, which also shewed a large increase.

Further investigations are in progress to determine the parts played by the β-radiation and the characteristic X-radiation from the gas in determining the total ionisation observed.

Results similar to those mentioned were also obtained with $Ni(CO)_4$ and AsH_3.

A constant temperature, porous plug experiment.

By W. A. Douglas Rudge, M.A., St John's College.

[*Received* 18 July 1910.]

The author has published an account of a porous plug experiment in the *Philosophical Magazine*, for July 1909. In this experiment a liquid gas was allowed to evaporate and expand slowly through a fine orifice and tube which acted as the plug, while the total thermal change produced during the expansion was observed. Dealing with a liquid gas it is obvious that the total thermal effect will be due to two causes, viz.:—

(1) The heat absorbed during evaporation of the gas.

(2) The thermal effect due to the passage of the gas through the plug.

As the only gas used so far in the experiment has been carbonic acid, (2) will be accompanied by an absorption of heat, so that the whole effect of the two factors will be to cause a reduction of temperature.

In the experiments referred to above, the temperature was in some cases allowed to fall, in others it was kept constant. Some experiments were conducted at temperatures below the critical point of CO_2 and others above it. The general method followed was that of allowing the gas to expand from a vessel immersed in a suitable calorimeter, and determining the thermal effect produced from the known heat capacity of the calorimeter and the change of temperature. In these experiments the contents of the calorimeter were heated by means of a current flowing through a manganin wire, curves being plotted of the rise in temperature:

(*a*) When the gas was not allowed to escape.

(*b*) During the escape of the gas.

From these the thermal effects during the escape of gas could be found. In one set of experiments the temperature was kept constant by regulating the strength of the current or the rate of flow of the gas.

The results of the experiments being rather variable, the method was modified, so that they might be conducted at a constant temperature, viz., that of melting ice.

The only gas available so far has been carbonic acid, contained in the small sparklets used for aerating water, but the method to be described can easily be carried out with any gas which is liquid at ordinary temperature.

The principle of the experiment is as follows:

If a vessel containing a liquid gas is opened slightly, the liquid will boil, and if the orifice is not large, the gas will boil away steadily, and the pressure of the escaping gas will be fairly constant. Heat of course will be absorbed in the process and the gas will become cool. Surround the vessel, however, with a mixture of ice and water, and the temperature will remain constant, and any heat absorbed by the expanding gas will be taken from the water, which being already at 0°C. will become partly frozen. If the amount of water frozen is determined, the amount of heat absorbed from it in order to keep the gas at a constant temperature can then be found.

The Apparatus (see figs. 1, 2). The essential parts are a small gas-tight chamber, *C*, in which the bulb containing the gas can be perforated, and the gas allowed to escape slowly through the small orifice, and then through a coil of fine-bore tubing, *T*. This

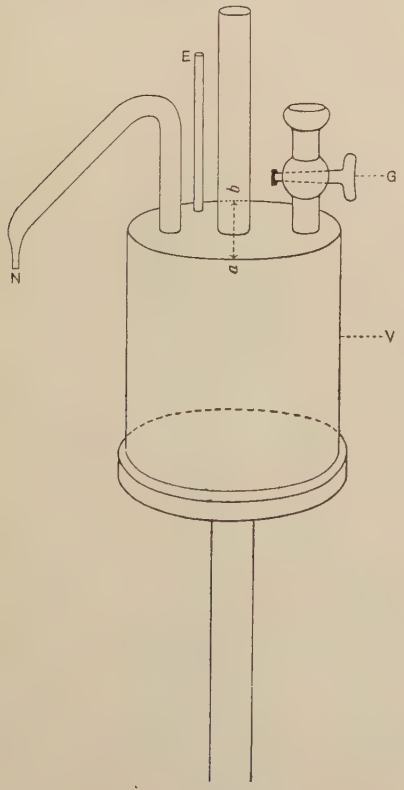
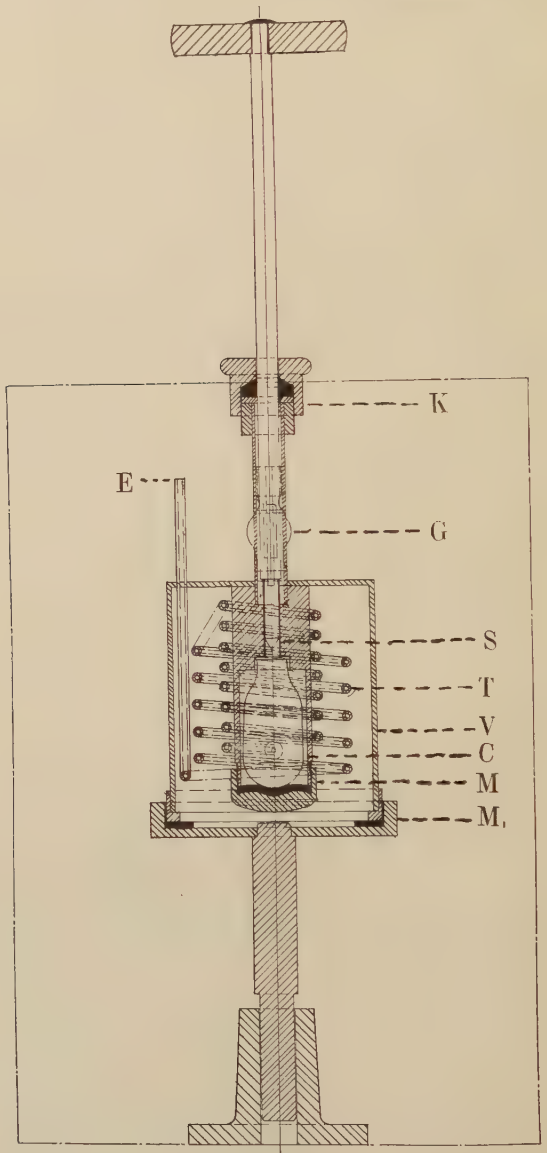


Fig. 1.

chamber and the spiral tube are arranged in a larger vessel, *V*, containing ice and water, and the alteration of the volume of the last is observed during the course of the experiment. The outer



Section C, D.
Fig. 2.

vessel acted as a Bunsen's ice calorimeter. The chamber C was made of brass and turned as thin as possible. The spiral tube was also of brass, 1 mm. internal diameter, the total of length tubing being nearly two metres. The screw S was of hard steel, packed air-tight by a stuffing-box at K. By unscrewing the bottom M the outer chamber could be nearly filled with a mixture of finely-ground ice and water. After filling, the apparatus was turned to the vertical position, and paraffin, previously cooled to 0°, poured in through G until it flowed freely out of the capillary tube N. The stop-cock was then closed. The whole was now placed in a large tin can, surrounded with pounded ice and water, and allowed to stand until the temperature had become stationary, and the paraffin just filled the capillary tube, more paraffin being poured in through G as required. On screwing down S, the cap of the bulb was pierced, but the conical end of the screw prevented the gas from escaping until it was turned slightly in the opposite direction. The end E of the spiral tube was attached to an india-rubber tube dipping under water, so that the rate of escape of the gas could be observed and controlled. This was easily done so that the escape of the gas occupied about 12 minutes. The heat absorbed by the gas, being taken from the plug and the mixture surrounding it, caused a certain amount of the water to freeze, and the increase in volume produced thereby caused paraffin to be expelled through N, into a weighed dish placed below it. From the density, and the volume of the paraffin expelled, the volume of the ice formed was determined, and by assuming the value of the density of ice as compared with water as ·907 and the latent heat as 80, the amount of heat involved was calculated in the usual way. In carrying out the experiments, the ice was first crushed and ground in a coffee mill. Several bulbs were weighed, marked with a number, and then placed in melting ice, in order to bring the contents to 0°. One of the bulbs was, after cooling, placed in the chamber; ice, water and paraffin were added as detailed to the calorimeter, and the whole immersed in the ice and water in the outer vessel. After the temperature had become steady, the apparatus was allowed to rest for from 10 to 30 minutes before puncturing the bulb; and, after the escape of gas was over, a further ten minutes were given, so that all the ice possible should be formed. If the escape of gas was too rapid, some solid CO_2 would be formed, and this took some time to evaporate. The paraffin expelled was collected in a weighed porcelain dish, the usual amount being 0·26 grams. The time involved in each experiment was about 45 minutes.

The plug proved quite efficient; for, on opening the calorimeter and inspecting the spiral, it was seen that ice was formed only round the chamber and along a part of the inner spiral, so

that the gas escaping from the end of the tube might be considered as being at 0°.

The heat evolved during the formation of the ice is taken to be equal to that absorbed by the evaporation of the liquid gas, together with that due to the absorption going on in the plug.

Taking 888 units as the amount of heat necessary to change the volume of a mixture of ice and water at 0° by 1 c.c., and I for the change in volume due to the ice formed, then

$$I \times 888 = \text{heat evolved.}$$

Let W = weight of gas escaping from the bulb, and L its latent heat at 0°, then

$$(I \times 888) - WL = \text{amount of heat absorbed by the plug.}$$

At 0° the vapour pressure of liquid CO_2 is 34·25 atmospheres, and assuming that the gas boils steadily away and also that the specific heat is constant under the conditions of this experiment, then

$$(I \times 888) - WL = W \times S \times (0 - t),$$

where t is the temperature to which the gas would have fallen, if it had been allowed to cool. The change in temperature per atmosphere difference will therefore be

$$t = \frac{(I \times 888) - WL}{W \times S \times P},$$

where P is the pressure in atmospheres.

In one particular experiment the following result was obtained:—

Weight of gas used	4·573 grammes.
Specific Heat of Gas	0·2044 „ *.
Latent heat at 0° C.	56·25 calories†.
Change in volume due to ice formed .	0·320 c.c.
Vapour pressure at 0° C. . . .	34·25 atmospheres‡.

Whence the fall in temperature per atmosphere difference in pressure is

$$t = \frac{(0{\cdot}320 \times 888) - (4{\cdot}573 \times 56{\cdot}25)}{4{\cdot}573 \times 0{\cdot}2040 \times 34{\cdot}25} = 0{\cdot}84 \text{ nearly.}$$

The results of the experiments are tabulated below. It will be seen that they are as uniform as might be expected in an experiment of this character when the amount of gas used is small. In the table the weights of bulb full and empty are given in columns (1) and (2), the weight of gas in (3), the amount of paraffin expelled in (4), the volume of the paraffin in (5), the heat absorbed by vaporisation of the liquid gas in (6), the total

* Deduced from Swann, *Roy. Soc. Proc.*, A, 553.
† Chappuis.
‡ Vellard, *Ann. Chem. Phys.* [7], x. 387.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
17·680	13·355	4·325	·245	·301	253·5	267·28	0·425
17·491	12·918	4·573	·256	·320	287·8	274·16	0·768
17·625	13·055	4·570	·264	·330	257·1	293	1·046
16·855	12·899	3·956	·23	·287	221·4	254·8	0·980
17·530	12·935	4·595	·2615	·301	258·4	267·3	·288*
17·625	13·025	4·600	·264	·330	258·7	292·5	1·01
17·730	13·14	4·590	·260	·325	258·2	288·6	0·874
17·588	13·075	4·513	·261	·325	253·7	288·6	1·017
17·298	12·86	4·438	·252	·315	249·6	279·7	0·866
17·772	13·23	4·542	·265	·331	255·5	293·9	1·118
17·600	13·019	4·581	·254	·317	257·8	281·5	0·671
17·632	13·098	4·534	·256	·320	255·1	277·6	0·653
17·654	13·069	4·585	·261	·326	258·4	289·4	0·904
17·700	13·257	4·543	·238	·297	255·6	263·7	0·23 *
17·132	12·883	4·249	·250	·312	249·1	277·1	0·819
16·985	12·771	4·214	·245	·308	237·0	272·9	1·046
17·485	12·904	4·581	·260	·325	257·1	288·6	0·918
17·532	12·965	4·567	·257	·321	256·7	285·0	0·825
17·534	13·012	4·522	·246	·3075	254·2	269·3	0·437
17·620	13·133	4·487	·238	·2975	252·4	264·2	·340*
17·309	13·008	4·301	·257	·321	242·5	285·0	1·240
16·975	12·925	4·050	·240	·300	227·8	266·4	1·128
17·670	13·068	4·602	·261	·325	258·9	288·6	·866
17·427	12·940	4·487	·270	·337	252·4	299·2	1·364
17·431	12·910	4·521	·267	·334	254·3	296·6	1·233
17·611	13·099	4·612	·259	·324	259·4	287·7	·825
17·309	12·738	4·571	·276	·342	257·1	303·7	1·329
17·487	12·998	4·489	·243	·304	252·5	266·7	·414
17·543	13·046	4·497	·260	·325	253·1	288·6	1·035
17·379	12·947	4·432	·261	·325	249·3	288·6	1·145
17·400	12·859	4·541	·257	·321	255·5	285·0	·860
17·612	13·046	4·566	·280	·350	256·8	303·8	1·370
17·550	12·937	4·513	·243	·304	253·9	269·9	·476
17·563	12·983	4·500	·267	·334	257·6	296·6	1·137
17·409	12·896	4·503	·262	·327	253·3	290·3	1·078
17·801	13·189	4·612	·260	·325	259·4	279·4	·873
17·489	13·013	4·476	·254	·317	251·8	281·5	·866
17·602	13·089	4·513	·270	·337	253·9	301·3	1·380
17·579	13·072	4·507	·248	·31	253·5	275·3	·635
17·521	13·040	4·481	·262	·327	252·1	290·2	1·111
17·623	13·023	4·600	·274	·342	258·7	303·7	1·312
17·600	12·986	4·614	·270	·337	259·5	299·2	1·160
17·597	12·997	4·600	·256	·32	258·7	287·4	·836
17·489	12·992	4·497	·256	·32	252·9	287·4	1·006
17·602	13·089	4·513	·261	·325	253·9	288·6	1·01
17·584	12·882	4·702	·259	·324	264·6	287·7	·673
17·625	13·105	4·520	·260	·325	254·5	288·6	1·000
16·843	12·910	3·933	·232	·29	221·2	257·5	1 06
17·601	13·116	4·485	·260	·325	252·3	288 6	1·06
17·584	13·087	4·497	·258	·322	252·3	286	·982
17·406	12·902	4·500	·260	·325	253·1	288·6	1·035
17·587	13·151	4·327	·251	·314	243·4	278·8	1·032
16·204	13·01	3·194	·176	·22	179·7	195·4	·451
17·600	13·087	4·513	·262	·327	253·9	290·3	1·061
17·589	13·019	4·370	·260	·325	257·0	288·6	·921
17·623	13·013	4·610	·266	·332	259·3	294·7	1·032
17·724	13·013	4·711	—	·342	264·6	303·7	1·140
17·540	13·080	4·490	—	·327	252·8	290·3	1·105
17·230	12·900	4·330	—	·308	243·5	273 5	·874
17·923	13·400	4·523	—	·354	253·8	314·4	1·737†
17·464	12·820	4·544	—	·33	255·9	293·0	1·081
17·330	13·03	4·300	—	·305	241·8	264·6	·664
17·730	13·203	4·427	—	·321	249·0	285·0	1·05
17·650	12·865	4·785	—	·34	268·5	300·5	·933
17·24	12·968	4·272	—	·323	240·3	286·8	1·326

* Some leakage occurred in these cases. † Stop-cock not properly closed.

thermal effect in (7), and the thermal effects per atmosphere difference in pressure in (8).

The figures given in the last column of the table are very far from being constant, so that it did not seem to be of very much importance to calculate the loss of temperature which would accompany the escape of the gas through the plug in each case, and therefore the average value for all the experiments has been determined. The average amount of gas contained in the bulbs is 4·478 grams, and the average heat absorbed by the plug is ·923 units per atmosphere difference of pressure. Now supposing the specific heat of the gas to remain constant during cooling, the amount of heat absorbed by the plug would be

$$H = M \times S \times t,$$

where M is the mass of gas, S the specific heat, and t the fall in temperature.

Taking the value for S as 0·2044 at 0°, then

$$t = \frac{H}{M \times S} = \frac{0{\cdot}923}{4{\cdot}478 \times {\cdot}2044} = 1{\cdot}008^\circ \text{ C.}$$

is the average cooling effected per atmosphere difference of pressure.

The last nine experiments were conducted without paraffin, for, as there was always a large excess of water, and the freezing never proceeded far from the inner spiral, it seemed that the water itself might be used to indicate the amount of expansion. The results from these experiments were somewhat higher than the general average, the cooling effect being 1·1900.

A weak point is the assumption that the pressure of the gas remains constant during the course of the experiment. This of course is not the case, though probably it is true during the evaporation of the greater part of the gas. The method of maintaining a constant pressure by the evaporation of a liquid gas, seems to be one which may prove useful in porous plug experiments, and it would be quite easy with a properly constructed apparatus to allow *a portion* only of the liquid gas to evaporate and by this means constant difference of pressure could be maintained.

By weighing the gas bottle before and after the experiments one could find the actual weight of the gas used. It should not be difficult to arrange for suitable pressure gauges to be attached to the opposite sides of the plug, so that the actual difference in pressure could be measured. A moderately strong steel bottle might be filled with any of the more easily liquefiable gases and the value of the thermal change determined for a number of substances.

The main feature of these experiments is the method adopted. By means of it, the thermal effect at constant temperature, due to the passage of a gas through a plug, can be determined.

Observations on the Surface Tension of Liquid Sulphur. By W. A. Douglas Rudge, M.A., St John's College.

[*Received* 18 July, 1910.]

(Plate I.)

If sulphur is heated carefully in a test tube it melts at about 115° C. to a pale mobile liquid which does not stick to the glass, but when the liquid is heated to about 160° it becomes viscous and then adheres to the side of the tube. On heating the sulphur on a glass plate it melts and the liquid drop will run over the surface of the glass without sticking anywhere if the temperature is about 120°—130° no mark being made upon the glass, that is, the liquid does not "wet" the glass.

It appeared to be of some interest to investigate the condition of liquid sulphur and in particular to make determinations of the surface tension, as at first sight it might appear that the liquid should behave as mercury does, and not rise in a capillary tube, but since the angle of contact is finite and positive this is not the case.

A series of experiments was first made in order to find the angle of contact of the liquid with the glass. The first method consisted in heating crystals of sulphur upon a $3'' \times 1''$ glass slip and observing the size and shape of the drop by a horizontal microscope, which could be rotated about its axis and also could be moved in two directions at right angles to each other.

Just as happens in the case of mercury a maximum thickness of the drop is attained, the thickness being about 1·455 mm., but this varied a little with different samples of sulphur.

The sulphur used in the investigation was purchased in the form of rhombic crystals, which from the slight odour had evidently been prepared from a solution of sulphur in carbon bisulphide. A quantity of these crystals was treated with sufficient carbon bisulphide to dissolve them and, after filtration, the crystals which separated first on slow evaporation were used for the experiment. Well-defined crystals were obtained.

A suitably sized crystal was placed upon the glass slip and the latter supported, with its surface horizontal, and heated by a small coil of platinum wire arranged underneath the slip, and provided with asbestos paper screens, the heating current being supplied by a few storage cells. With the aid of a rheostat in the circuit, the heating could be controlled.

The sulphur was seen to melt sharply and to gather itself into a drop which was a segment of a sphere if the quantity of material was small, if a large amount of sulphur was used then the drop was flat over the central portions. Drops of different sizes presented the same outline as long as they were small.

Fig. 1 shows a group of these drops under a magnification of about 5 diameters.

If the drops were allowed to solidify, the shape did not perceptibly alter, the contact between the drop and the glass being sharply defined.

On raising the temperature the shape of the drop did not alter until 180° was reached, when it flattened and remained in this condition until 260° when it flattened still further.

Figs. 2, 3, 4 show the appearance of the drop at 130°—190° and 265°.

A curious fact is that on cooling down from 265° the shape of the drop does not alter, but having once become flat it remains so, and the same thing is seen on cooling from 160°. By heating to the higher temperatures the sulphur evidently "wets" the glass, and modifies the surface of the latter in some way, so that even on cooling down to the solidifying point and again melting, it still sticks. The sulphur has not itself altered, for if a portion of a drop which is sticking is jerked out on to a part of the glass free from sulphur and at a temperature of 130°, it slides about just as a drop of freshly-melted sulphur will. Solidification does not influence the wetting, as a drop may be melted and cooled many times and it will run over the hot surface of the glass if the temperature has not been raised above 180°.

In order to get exact values for the temperatures at which the changes in form occurred, the glass slips were heated to definite temperatures by floating upon heated mercury. The presence of the mercury vapour, however, very materially altered the nature of the drop owing to the combination which occurred between the mercury and sulphur. The drops were no longer portions of spheres and even at temperatures just over 115° a change in form was seen. The sulphur now wets the glass, and Fig. 5 shows how it curves so as to run along the surface. The outer skin of the drop is of course composed of mercury sulphide. At a temperature of 125°—130° the drop assumes the form shown in Fig. 6.

A series of measurements of the angle between the tangent to the surface of the drop at the point of contact and the glass plate was taken as indicated by the intersection of the straight lines in the figures. To do this the microscope was adjusted with the cross wire parallel to the plate, and the position of the vernier noted. The microscope was then turned about its axis until the

cross wire was a tangent to the drop at the point of contact and the new position noted. The difference of the vernier readings gave the angle of contact of the drop with the surface.

The following are a few typical readings taken on different drops whose diameters varied from ·5 mm. to 12 mm.

TABLE I.

Temperature	1st Reading	2nd Reading	Angle
130° C.	273·0	209·5	63°·5
127° „	275·2	218·0	57°·2
132° „	209·5	147·3	62°·2
120° „	209·6	150·35	59°·25
			Mean 60°·05

TABLE II.

Temperature	1st Reading	2nd Reading	Angle
185° C.	210·2	165·5	44°·7
190° „	230·5	187·9	42°·6
195° „	227·6	174·6	43°·0
190° „	216·9	172·6	43°·3
			Mean 43°·4

TABLE III.

Temperature	1st Reading	2nd Reading	Angle
256° C.	209·6	173·6	26°·0
261° „	210·3	182·7	27°·6
254° „	210·0	183·7	26°·3
			Mean 26°·6

Small crystals of sulphur were placed upon the glass slips and the latter heated in a small air oven up to the temperature indicated, and in the case of the last two tables the angle was determined after the drop had solidified. In the case of the first table the measurements were made on the liquid drop. At about 265° the sulphur ignited, but this did not have much influence on the shape of the drop.

Capillary Experiments.

The surface tension was determined from the rise of the liquid in a capillary tube using the formula:

$$T = \frac{rphg \cos \theta}{2},$$

where
r = radius of tube,
ρ = density of liquid,
h = height of liquid in cms.,
θ = angle of contact.

The density of the liquid sulphur was determined between the temperatures of 123° and 154° by ascertaining the loss in weight of a glass plummet, after Mathiessen's method.

The plummet was suspended by a quartz fibre from the arm of a delicate "Westphal" balance, and the loss in weight in water at different temperatures found, in order to determine the coefficient of expansion, so that the volume of the glass at the temperature of the liquid sulphur could be calculated. The weight of the plummet in air at 24° was 7·725 grms., and the loss in weight in water at the different temperatures was found by adding "riders" to the arm of the balance.

Table IV.

Temperature of water	Loss in weight
	grms.
24° C.	3·0935
47° ,,	3·0670
60° ,,	3·0525
68° ,,	3·0408

From these values, the coefficient of expansion of the glass was:

0·000026 nearly.

The experiment was then made of weighing the plummet in liquid sulphur at different temperatures.

TABLE V.

Liquid Sulphur.

Temperature of liquid	Loss in weight
	grms.
123° C.	5·622
133° „	5·590
141° „	5·572
133° „	5·587
149° „	5·555
133° „	5·587
154° „	5·541
158° „	5·53 viscous
133° „	5·591

By aid of Table IV the volume of the plummet at 60° was found from the density of water at that temperature, and assuming that the expansion was uniform between 60° and 133° the volume at the latter temperature could be calculated. At 133° the sulphur was perfectly fluid.

Mean loss in weight at	133°	5·5888 grms.
Density of water at ...	60°	0·98339
Volume of glass at ...	60°	3·104 c.c.
Volume of glass at ...	133°	3·1099 „
Density of sulphur at	133°	1·861

In order to find the capillary constant, some thermometer tubing was used and, after cleaning in the usual way, was allowed to stand in a test tube full of carbon bisulphide until wanted.

The sulphur was placed in a test tube, about 2 cms. in diameter, and melted by heating in a large beaker containing glycerine. It may be mentioned that a glycerine bath is a very convenient means of heating substances which have to be examined at temperatures up to 280° as the glycerine does not boil until about 290°, and if clean and free from organic matter remains quite clear.

The heating was effected by a current sent through a coil of platinum wire immersed in the glycerine.

When the sulphur was melted the capillary was dried by blowing air through it and then immersed in the liquid, and the difference in level between the surface of the sulphur in the test tube and that of the sulphur in the capillary found by a table cathetometer.

Considerable difficulty was experienced in getting a series of consistent results, for with a particular tube the difference in level at practically similar temperatures varied considerably, and the only satisfactory results were obtained by forcing the column of liquid down by blowing air in at the top and noting the height to which the sulphur rose on withdrawing the pressure. Raising the liquid above the level by suction did not answer nearly so well. After a set of observations, the tube was cut at the point where the meniscus stood and measured with a reading microscope in the usual way.

TABLE VI.

Mean diameter of tube 0·103 cms.

Upper Reading	Lower Reading	Height of liquid
		cms.
15·745	15·522	·223
15·455	15·240	·215
15·894	15·670	·224
15·461	15·230	·231
15·465	15·235	·230
15·861	15·600	·261
15·555	15·268	·287
15·410	15·120	·290
15·545	15·260	·280
15·580	15·365	·215
15·505	15·245	·260

If we take the mean of the whole we get ·246 cms. for the height of the column of liquid sulphur, and, calculating from the approximate formula

$$T = \frac{r_1 \rho_1 g_1 h_1 \cos\theta_1}{2},$$

we get

$$T = \frac{\cdot 103 \times 1\cdot 861 \times 980 \times \cdot 246 \times \cdot 5}{2}$$

$$= 11\cdot 56 \text{ nearly}^*.$$

It might be expected that considerable variation of the height of the liquid at different temperatures would occur, especially when

* Similar results were obtained with other tubes, but for some reason the sulphur showed greater freedom of movement in this tube.

the temperatures were reached at which the liquid becomes viscous and wets the tube, but this was not the case, although a change in the shape of the meniscus was seen, it becoming deeper. Beyond 160° the liquid was viscous and considerable pressure was required to force it up or down the tube. If forced up, it remained up, but if forced down it very slowly rose to its old level. Between the temperatures of 122° and 154° the height of the liquid was practically constant. If a tube had been heated in the sulphur up to 180° it was quite useless for experiments at lower temperatures. In one case on heating the sulphur up to its boiling point the liquid rose 2·3 cms. in the capillary, but remained at this height and did not fall to a lower level on cooling. No change was seen at those temperatures at which the values of the angle of contact changed.

The temperature at which the changes occurred was obtained by surrounding the bulb of a thermometer with a closely fitting cylinder of copper, cut away above so as to expose a portion of the thermometer bulb, the copper rod being heated by a burner and the thermometer screened from direct radiation by asbestos board. A small speck of sulphur was placed on the bulb and observed through the microscope.

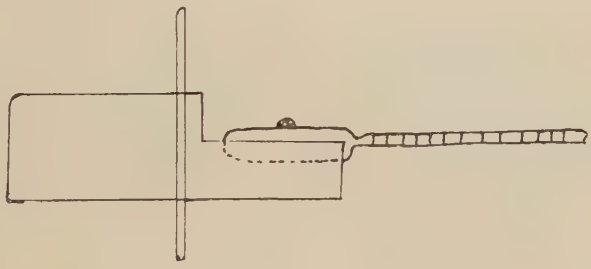


Fig. 7.

The temperature of liquefaction was 115°.

The temperature of the 1st change in angle 185°*.

The temperature of the 2nd change in angle 256°*.

Just above the last temperature the sulphur ignited.

As already mentioned the presence of mercury vapour modified the angle of contact, and some experiments were made to ascertain whether the surface tension was also changed by presence of mercury vapour.

With this object two test tubes, one containing sulphur and the other mercury, were heated in the glycerine bath. A capillary tube was placed in the sulphur, and then withdrawn,

* These are the mean values of a number of determinations.

so as to leave some sulphur in the tube with a drop hanging. The length of the capillary column and the diameter and depth of the drop were measured. The tube was then quickly transferred to the test tube containing the mercury. The drop flattened and changed its shape but the height of the column did not alter, while a skin of mercury sulphide rapidly formed.

Attempts were made to find the angle of contact by causing liquid sulphur to rise up in a hollow glass sphere until the surface was level all over and the meniscus disappeared at the edge.

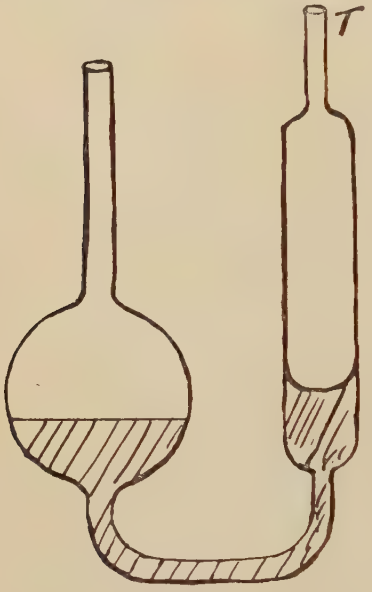


Fig. 8.

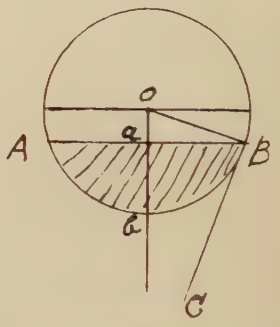


Fig. 9.

A tube was fashioned of the shape shown, the bulb being made as spherical as possible, and heated in the glycerine bath to 135° C.

By forcing air into T the sulphur could be made to rise in the bulb and the height noted when the surface appeared level.

If AB is the level of liquid, OB the radius of the sphere and BC the tangent at B, then ABC = angle of contact θ.

Let $ab = y$, the depth of the liquid, and $OB = r$ the radius of the sphere, then

$$\cos\theta = \frac{r-y}{r}.$$

A series of observations with a bulb of radius 1·625 cms. gave the following results:

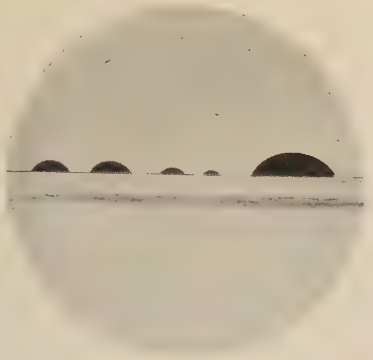


Fig. 1.

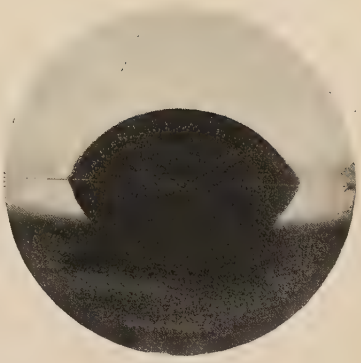


Fig. 2.

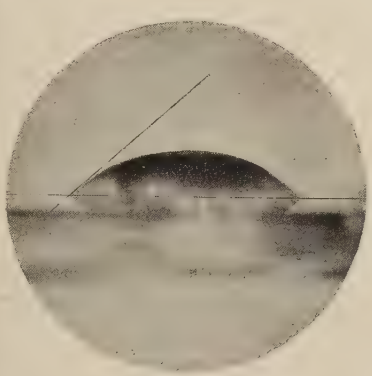


Fig. 3.

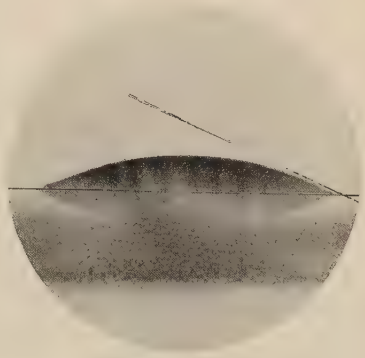


Fig. 4.

Fig. 5.

Fig. 6.

SULPHUR

TABLE VII.

Radius of sphere = 1·625 cms.

Values of y	$\cos\theta$	θ
0·73	0·544	51°·3
0·80	0·508	59°·33
0·78	0·521	58°·36
0·81	0·500	60°·0
0·84	0·482	61°·13
0·90	0·434	64°·15
		Mean 60°·13

Quite fair results may be obtained by melting sulphur in test tubes about 1·2 cms. in diameter, using different amounts, and measuring the thickness of the solidified material when the upper surface was flat all over*.

The diameter and thickness of the drops solidified upon the glass slips could also be used for making similar measurements.

Not very much error can be made in assuming that the angle of contact is about 60°. It is very essential that the bulb should be quite clean and also not heated for long periods in contact with the sulphur even if the temperature is well below 150°, as both the glass and the sulphur seem to change after prolonged heating.

It was somewhat difficult to secure satisfactory photographs, when the magnification was large. The lower portion of the figures is formed by reflections in the surface of the glass.

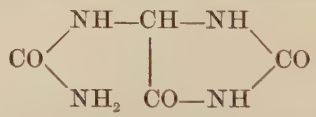
* The sulphur occupied only the rounded end of the tube.

A method of characterising certain Ureides. By H. J. H. Fenton, Sc.D., F.R.S., Christ's College, and W. A. R. Wilks, B.A., Gonville and Caius College.

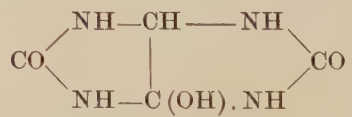
[*Read* 28 November 1910.]

Reference has been made, in previous communications, to a substance having the empirical formula $C_{11}H_8O_4$, provisionally termed methyl-furil, which is obtained by the action of sulphurous acid on bromomethylfurfural and an account has been given of its applications as a reagent*. It was shown that this reagent in presence of hydrochloric acid, or phosphorus chlorides, gives an intense blue colouration with urea and with certain ureides, and that it serves as an exceedingly delicate test for these compounds.

The present authors have now made a further study of this reaction by extending the observations to many additional ureides of known constitution, and it would appear that the test, when carried out in the manner described below, gives positive results for all ureides containing the open chain—NH—CONH$_2$ but gives negative results with those having a cyclic structure. Thus, for example, positive results are obtained with urea, monomethylurea, benzylurea, semicarbazide, oxaluric acid, biuret, and hydantoic acid; but negative results with parabanic acid, hydantoin, oxamide, succinamide, and with sym. and unsym. dimethylurea. In this connection, it is of interest to observe that allantoin gives a very well-marked positive reaction, a circumstance which affords evidence in favour of the older formula proposed by Grimaux:



rather than the "hydroxyacetylene-diurein" formula



which has been more generally accepted†.

The method adopted in applying this test consists in mixing together minute quantities of the substance to be examined and the reagent, on filter paper, and adding a drop of fuming hydrochloric acid. In the case of the substances referred to, an intense blue spot appears after a few seconds.

* Compare, for example, Fenton, *Trans. Chem. Soc.*, 1903, 187; *Cambridge Philos. Soc.*, 1906 (13), 298.

† Compare H. Biltz, *Ber.* 1910, 2002.

A note on the action of aluminium chloride on benzene. By Annie Homer, Newnham College.

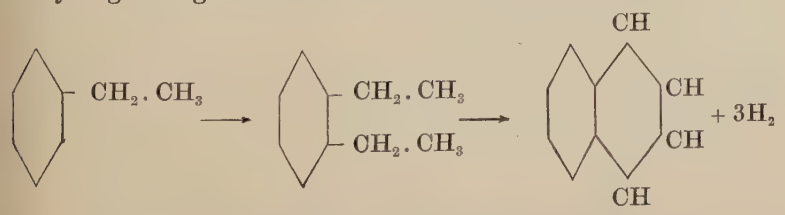
[*Read* 28 November 1910.]

Friedel and Crafts* have shown that aluminium chloride reacts with benzene to form toluene, xylene, ethyl benzenes and diphenyl. At a later date† they made the observation that if a current of dry oxygen were passed for a long time through a mixture of benzene and aluminium chloride kept at the boiling point of the benzene, a slight reaction took place whereby phenol was formed together with derivatives of phenol which could not be distilled.

In the present investigation pure dry benzene was treated with 25 per cent. of its weight of aluminium chloride. The flasks containing the mixture were fitted with reflux condensers to which were attached calcium chloride tubes; the flasks were heated to 100° C. for periods of 10 to 14 days. After treatment of the residues with water and hydrochloric acid the oily layer consisting of unchanged benzene and the products of the reaction was removed, dried over calcium chloride and fractionally distilled. Besides the alkyl benzenes and phenol previously obtained by Friedel and Crafts the following fractions were isolated:

Fraction i. (below 160°/10 mm.) consisted of phenol and naphthalene. The naphthalene was recognised by its appearance, odour, melting point (81°), and by the melting point of its picrate (147°). Mixture of the substance with naphthalene and of its picrate with naphthalene picrate caused no change in the respective melting points, thus proving the identity of the substance with naphthalene.

The formation of naphthalene from benzene is interesting, and can be explained on the assumption that the ethyl benzene first formed is changed under the influence of the aluminium salt to diethyl benzene, which is then condensed to naphthalene by a dehydrogenising effect of the aluminium chloride. Thus:



* *Compt. rendu*, 1885, c. 692.

† *Ann. Chim. Phys.* 1888 [6], t. xiv. 433.

Naphthalene was isolated from the products obtained in several experiments conducted under the above conditions, but none was isolated in an experiment in which the reaction was carried out for two days in sealed tubes at 180°.

Fraction ii. (between 160° and 200°/10 mm.) was a colourless oil which rapidly turned purple in the air. Analysis showed that it contained about 5 per cent. of oxygen, but no concordant results were obtained. The fraction was probably a mixture of substances which could not be separated by fractional distillation. *Fraction iii.* (212°/10 mm.), *Fraction iv.* (240°/10 mm.), *Fraction v.* (260°/10 mm.) were oils, *Fraction vi.* (above 300°/10 mm.) on cooling set to a hard brittle mass.

These fractions, contrary to Friedel and Crafts' observations, were hydrocarbons and not phenol derivatives. Analysis gave:

Fraction iii.	C = 92·6 per cent.	H = 7·43	M.W. = 170.
„ iv.	C = 92·9 „ „	H = 7·2	M.W. = 210.
„ v.	C = 92·4 „ „	H = 7·1	M.W. = 240.
„ vi.	C = 92·3 „ „	H = 7·0	M.W. = 270.

The hydrocarbons do not give readily crystallisable substitution products and they cannot be easily oxidised. At present no suggestion can be offered as to their constitution, although some of their nitration products are being investigated. It is extremely probable that the difficulty of the problem has been increased by secondary reactions between the primary products of the action of aluminium chloride on benzene and the phenol and oxygen containing compounds (Fraction ii.) formed by the interaction of the oxygen of the air with the benzene and aluminium salt. An attempt to elucidate the problem by the preparation of the oxy compounds in greater quantity was made, but without success. A slow current of dry air was passed through the reaction mixture, but an examination of the products yielded only a small amount of phenol and a dark viscous substance which could not be distilled at the temperature at which glass melts; there were none of the Fractions ii. to vi. present in the products.

Thus the action of aluminium chloride on benzene in the presence of a small supply of air proceeds slowly and the relative amount of benzene changed is small. The products of the reaction are alkyl benzenes, naphthalene, phenol and a series of hydrocarbons. If a slow current of air be continuously passed through the reacting mixture the only products are phenol and dark non-distillable products.

The Radium-Content of Salts of Potassium. By JOHN SATTERLY, D.Sc. (Lond.), B.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 28 November 1910.]

In 1907 Mr N. R. Campbell*, working at the Cavendish Laboratory, discovered

(1) that the salts of potassium were radio-active;

(2) that they emitted β-rays of velocity less than the β-rays of uranium;

(3) that the activity of potassium measured by its ionising power was about $\frac{1}{1000}$ of that of uranium as measured by the ionisation caused by the β-rays from that substance.

To assure himself that the activity was not due to radium, thorium, or actinium, Campbell tested the salts for emanation. The following passage taken from his paper gives his method and results. "The sample of potassium sulphate used was tested for an emanation. A saturated solution of the salt in water was stored in a closed vessel for four weeks. At the end of that period the air above the solution was drawn into a testing vessel. No increase in the ionisation was observed. To indicate the sensitiveness of the test, it may be remarked that one-thirtieth part of the emanation in a volume of Cambridge water equal to that of the solution would have been detected with certainty. The presence of radium, thorium, or actinium is negatived decisively by this test."

It will be noticed that the air above the solution was drawn off and tested; the solution was not boiled, and air bubbled through it to clear out any emanation generated in the four weeks of standing. No doubt if the salt contained radium some of the generated emanation would be in the air above the solution after four weeks, but the main volume of the emanation would be dissolved in the solution, and thus Campbell's method would overlook the main volume of emanation generated.

Since Campbell's first experiments many other workers have gone into the question of the activity of potassium, but this point seems to have been generally overlooked. Elster and Geitel†, however, detected a slight activity on a negatively charged wire placed for a time above some carnallite, but they were not sure whether the active deposit came from radium emanation given off by the salt or from the radium emanation in the air.

The author has determined‡ that if a litre of Cambridge tap water, fresh from the tap, is boiled and air bubbled through, the

* *Camb. Phil. Soc. Proc.*, XIV. Mar. 1907 and Nov. 1908.

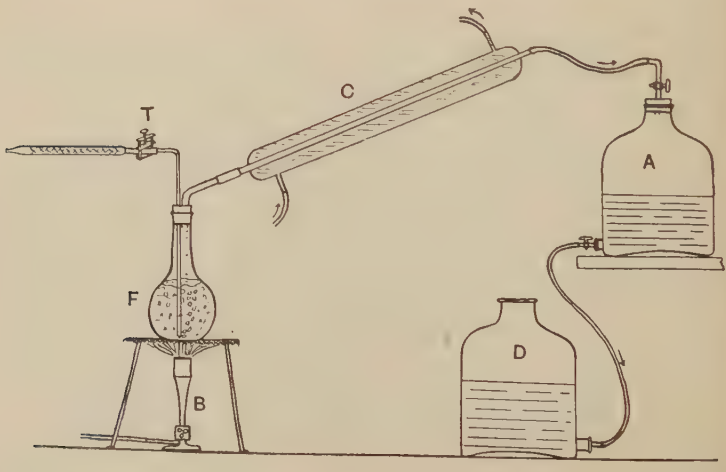
† *Physik. Zeitschr.* XI. 1910, p. 279.

‡ *Camb. Phil. Soc. Proc.*, XV. June 1910.

amount of radium emanation given off is that which would be in equilibrium with 130×10^{-12} gm. radium. Assuming in Campbell's comparison experiment that the relative concentrations of the emanation in the air above the liquid and in the liquid were the same in the two cases of the solution of potassium salt and the tap water, it follows that the amount of radium in the potassium solution was less than 4×10^{-12} gm. per litre.

It was to measure the absolute amount of radium in potassium salts that the following experiments were made.

The apparatus used for extracting the emanation from the solution is shown in the figure. The solution was placed in a litre flask F fitted with a cork and two tubes. The larger tube served as an outlet and communicated to a Liebig's condenser C placed on the slant to allow the condensed water to run back into the flask. The other end of the condenser tube was joined to a large bottle A which, in conjunction with another bottle D, served to aspirate air through the solution. The air was admitted into the solution through a tube containing coconut charcoal. The charcoal would absorb any emanation that might exist in the air of the room. When heat was first applied to the solution the taps of the bottle A were opened, and when the solution had been boiling for some time the clip T was also opened. The flow of water from A to D now sucked a rapid stream of air through the solution and all its generated emanation was removed and stored in the air collected in the bottle A. To test the amount of this emanation a testing vessel was exhausted and filled with the air in A. The "leak" in the testing vessel was then measured by a Dolezalek electrometer. The identity of the emanation with radium emanation was shown by the gradual increase of the leak for three hours.



In order to express the radium-content of the solution in terms of radium a precisely similar experiment was performed with a radium solution of known strength. The solution used contained $1{\cdot}57 \times 10^{-9}$ gm. of radium as radium bromide and a day's accumulation of emanation from this solution afforded a "leak" of 20·0 cms. per minute*. Then if a certain solution of a potassium salt yields in a day emanation which gives rise to a leak l cms. per minute the radium-content of the solution

$$= \frac{l}{20{\cdot}0} \times 1{\cdot}57 \times 10^{-9} \text{ gm. radium.}$$

The salts of potassium used were the chloride, sulphate and nitrate, and some carnallite ($KCl.MgCl_2 6H_2O$) from Campbell's stock of salts, also the sulphate, carbonate and nitrate, as supplied by Kahlbaum. The wood ashes mentioned by Campbell were also tested. Strong solutions were made up in litre flasks using distilled water†. After each boiling the solutions were allowed to stand for about a week before retesting. The results are indicated in the table on page 70.

The mean result is that one gram of potassium salt contains about 3×10^{-14} gm. of radium; the radium-content does not seem to bear any ratio to the percentage of potassium in the salt. It is probably a mere accidental impurity.

It is worthy of mention that a solution of sodium carbonate containing 196 grammes of anhydrous salt (Kahlbaum) was tested in the same way for emanation but none was found after a seven days' standing.

Since the activity of uranium is about one two-millionth of that of radium and Campbell found that the activity of potassium is about one-thousandth of that of radium, it follows that if the activity of the potassium salt were solely due to radium $\cdot 5 \times 10^{-9}$ gm. of radium per gm. of salt would be required. My experiments show that the actual radium-content is only about one ten-thousandth of this, so that Campbell was quite right in declaring that potassium itself was radio-active.

My best thanks are due to Professor Sir J. J. Thomson for his kindly interest in the experiments.

* *Camb. Phil. Soc. Proc.*, xv. p. 543.

† The distilled water was tested and found free from radium.

Salt	Mass used. (gm.)	Period standing. (Days)	Total leak when air passed from bottle into testing vessel	Normal air leak taken just before	Leak due to the emanation generated in the given period	Leak due to the emanation that would be generated* per day	Amount of radium contained in the sample of salt	Amount of radium contained per gram of salt
							gm.	gm.
(1) KCl	200	7	1·23	1·00	·23	·053 } ·052	$4·2 \times 10^{-12}$	$2·1 \times 10^{-14}$
		8	1·34	1·10	·24	·052 }		
(2) K_2SO_4	215† 105	7	1·58	1·10	·48	·11 } ·11	$8·6 \times 10^{-12}$	$8·2 \times 10^{-14}$
		8	1·7	1·2	·5	·11 }		
	110	8	1·20	1·15	·05	·01 } ·015	$1·3 \times 10^{-12}$	$1·2 \times 10^{-14}$
		7	1·35	1·25	·10	·02 }		
(3) KNO_3	252	8	1·7	1·1	·6	·12 } ·10	8×10^{-12}	$3·2 \times 10^{-14}$
		11	1·5	1·1	·4	·08 }		
(4) Carnallite	160	7	1·53	1·13	·40	·09 } ·11	9×10^{-12}	$5·4 \times 10^{-14}$
		11	1·95	1·20	·75	·14 }		
(5) K_2SO_4	186	7	1·67	1·14	·53	·12 } ·11	8×10^{-12}	$4·4 \times 10^{-14}$
		12	1·65	1·10	·55	·10 }		
(6) K_2CO_3	183	6	1·20	1·15	·05	·01 } ·01	1×10^{-12}	$·5 \times 10^{-14}$
		7	1·12	1·05	·07	·01 }		
(7) KNO_3	162	6	1·30	1·15	·15	·04 } ·03	3×10^{-12}	2×10^{-14}
		6	1·2	1·1	·1	·03 }		
(8) Ash Mixture	276‡	10	1·5	1·1	·4	·08 } ·07	6×10^{-12}	——
		10	1·4	1·1	·3	·06 }		

Remarks. (1), (2), (3), (4) were from Campbell's stock of salts; (5), (6), (7) were fresh from Kahlbaum.

* The numbers in this column were obtained from the numbers in the next column to the left by using the "growth" curve of radium emanation. (See also Kolowrat's tables, *Le Radium*, 1910, pp. 193—195.)

† The 215 gm. were dissolved in hot water. On cooling 105 gm. crystallised out and a slight sediment was deposited. The solution (containing 110 gm.) was poured off from the crystals into another flask, and the crystals (105 gm.) were redissolved to form another solution.

‡ 276 gm. of Campbell's ash mixture were taken and boiled with water and a little hydrochloric acid. On cooling the mixture was filtered. The solution was used in the tests. After the completion of the tests the solution was treated with sulphuric acid,

On the Inheritance of the Yellow Tinge in Sweet Pea Colouring. By M. G. Thoday (Sykes), Girton College, Fellow of Newnham College, and D. Thoday, M.A., Trinity College, Demonstrator of Botany in the University of Cambridge.

[*Read* 14 November 1910.]

Some experiments were started by one of us in 1906 with the object of investigating the nature and inheritance of the yellow tinge in scarlet, salmon, and deep cream sweet pea flowers. Several crosses were made and the offspring grown as far as the F_2 generation. The results from Queen Alexandra × Dorothy Eckford seemed most suggestive, and the inheritance of various F_2 individuals was investigated in F_3 and F_4. For the experimental work of 1910 and for the conclusions deduced from the results we are jointly responsible.

The seeds from which the parent plants were grown were obtained from Messrs Eckford. We are indebted to Mrs Sykes, Rossett, Denbighshire, and Mr Allington Hughes, Gresford, Denbighshire, to the Royal Holloway College, Girton College, and the Experiments Fund of the Cambridge University Botanic Garden, for ground in which to grow our plants; also to Dr M. Benson and Miss E. Welsford, Royal Holloway College, and Mr J. Seabourne, gardener, Rossett, for assistance in harvesting and planting out.

Results from Various Crosses.

The crosses made and the F_1 forms obtained from them were as follow:

Queen Alexandra—bright scarlet Dorothy Eckford—white	King Edward*—magenta with a slight crimson flush in the standard.
Queen Alexandra—bright scarlet Miss Henrietta Philbrick—clear blue self-coloured	Purple Invincible.
Miss Henrietta Philbrick—clear blue self-coloured Dorothy Eckford—white	Blue with a dingy standard.
Dorothy Eckford—white Henry Eckford—deep salmon	Bluish pink with a slight salmon flush in the standard.

* It must be clearly understood that only the parent plants are named varieties in the florists' sense; when plants among the offspring are described by florists' names it is merely intended to indicate apparent identity in flower colour and we do not wish to imply complete resemblance of form, etc.

The F_2 from *Queen Alexandra* × *Miss Philbrick* was far too complex for any hope to be entertained of a satisfactory analysis.

From *Dorothy Eckford* × *Henry Eckford* various pale magenta, salmon, white, pale cream and deep cream forms were obtained similar to those occurring together with reds in F_2 from Dorothy Eckford × Queen Alexandra. It was hoped that this cross would prove the most interesting, but its offspring set seed so badly that it was abandoned.

It is remarkable that the F_1 forms from the first and the last two crosses in the list given above are all slightly bicoloured flowers. The blue parent in Miss Philbrick × Dorothy Eckford was clearly self-coloured; crossed by Dorothy Eckford it gave a bicolor blue F_1, and the F_2 generation consisted only of forms resembling the two parents and the F_1. The tinge in the standard is somewhat pinkish and can hardly be called yellow as it is in the other two cases; but since it turns up each time in F_1 it appears probable that in all the crosses it is brought in by Dorothy Eckford and is a dominant character. This is somewhat surprising as it is found that all the other yellow tinges are recessive. Compared with these other recessive tinges this dominant tinge is so slight that it is necessarily neglected. It nevertheless in all probability confuses the issues in the Queen Alexandra × Dorothy Eckford cross, by adding to the difficulty, great enough in itself, of distinguishing between certain closely similar forms.

Offspring from Queen Alexandra × Dorothy Eckford.*

I. *Ratio of reds : pinks : whites.*

(*a*) The proportion of coloured forms to whites (including creams) approximates to 3 : 1. In F_2 there were 85 reds and pinks to 22 whites and creams†. The proportion is better shown in later families. All the families in F_3 and F_4 from magenta parents which gave red, pink, and white forms, taken together, gave 149 reds and pinks to 50 whites and creams. Similarly the largest pink families gave 37 : 12 and 32 : 10. Thus on the ordinary hypothesis that two factors are concerned in producing colour‡, *C* and *R*, either *C* or *R* must have been present in Dorothy Eckford.

(*b*) The proportion of pinks to reds suggests that the greater intensity of colour in the reds is dependent not on a single factor as in the cases hitherto investigated, but on the concurrence of two independently inherited factors. In the former case there should

* Both forms are hooded, Dorothy Eckford markedly so.

† Owing to unfortunate weather only this small number of F_2 plants, 107 in all, were obtained from several hundred seeds sown.

‡ Bateson, W., Saunders, E. R., Punnett, R. C., *Roy. Soc. Proc.*, B, Vol. LXXVII. p. 236, and *Reports to the Evolution Committee*, III., and following.

be 3 reds to 1 pink, in the latter 9 reds to 7 pinks. The numbers actually found and those to be expected are as follow:

In F_2	51 reds : 34 pinks
In F_3 and F_4 families from magenta parents	81 reds : 61 pinks
Total	132 reds : 95 pinks
Expectation 9 : 7	128 *reds* : 99 *pinks*

The same high proportion of pinks is shown by most of the families from red parents.

If this interpretation is correct some of the pinks when crossed together should give reds. It is hoped that this may be tested later.

II. *The yellow factors.*

The various forms which were distinguished in F_2 and the following generations are given in the list:

Pink Forms.

Blue pink .....pale magenta.
Blue pink bicolor .....pale magenta, with salmon flush in standard.
Blue pink tinged .....pale magenta, with slight salmon flush.
Helen Lewis (bicolor) .....wings pale magenta with slight salmon flush, standard salmon.
Salmon pink .....salmon pink.
Deep salmon (St George)...deep salmon, standard deeper.

Red Forms.

King Edward .....magenta, with slight crimson flush in standard.
King Edward bicolor .....magenta, with scarlet flush in standard.
Pale Queen Alexandra.....pale scarlet.
Deep Queen Alexandra ...deep scarlet.

White and Cream Forms.

White
Pale cream...some showing a difference between standard and wings.
Deep cream.

The pink varieties are more easily distinguished than the reds, as the various shades of yellow stand out more clearly on the paler ground.

Among the red forms the F_1 *King Edward,* magenta with a slight crimson flush in the standard, cannot be accurately separated from a form, referred to as *King Edward tinged,* in which a similar slight crimson flush tinges the whole flower. *King Edward bicolor,* with wings of a pure magenta, has a bright scarlet standard. Several

slightly different forms are collected together under the name *pale Queen Alexandra*, of which the most easily distinguished is a fine self-coloured pale scarlet; the others are pale scarlet with a more or less distinctly deeper standard, intermediate between *King Edward tinged* on the one hand and deep Queen Alexandra on the other. *Deep Queen Alexandra* is probably identical in colour with the parent form; it is deep scarlet all over, the standard appearing yet somewhat deeper than the wings.

Among the pinks the forms arrange themselves more distinctly into pairs, one member of each pair being markedly bicoloured. *Blue pink* is a pale magenta flower, corresponding in the pale series to King Edward in the red series. It is almost a self-coloured pea, but sometimes the standard appears to have a less bluish tinge than the wings. *Blue pink bicolor* has wings like blue pink but a bright salmon standard, its appearance suggesting that it corresponds to the red King Edward bicolor. The second pair of forms consists of *Blue pink tinged* and *Helen Lewis*. The former, which is not easily distinguished from Blue pink, is pale magenta with a slight salmon flush all over the flower, apparently self-coloured; Helen Lewis is a bicolor having wings like Blue pink tinged but a salmon standard. *Salmon pink* is a beautiful self-coloured pea, at once recalling the self-coloured pale Queen Alexandra; some examples were almost flame colour and probably represent a distinct type. The deep salmon form called *St George* resembles the florists' St George and is bicoloured, with its wings deeper than salmon pink and its standard a still deeper salmon, almost orange. Of this variety also two forms were distinguished, one with its wings not quite so yellow as the other; these two types may probably be looked upon as the respective bicoloured forms of the two kinds of self-coloured salmon pinks.

The *whites* are easily separated from the *deep creams*, which recalled the Hon. Mrs Collier in shade. There were several *pale creams*, some almost white, and self-coloured, others bicoloured, having a standard verging towards deep cream.

Microscopical evidence. The examination of the cells of the flower under the microscope is not always entirely satisfactory as a method of distinguishing between the various forms, but it throws some light on the nature of the yellow tinge associated with the different factors.

The yellow colouring is found (*a*) as a yellow tinge in the sap colour, that is, the sap instead of being magenta is scarlet or salmon; (*b*) as golden yellow plastids.

In three of the forms the yellow tinge is entirely due to sap colour. These three are a pale Queen Alexandra, Salmon pink, and one of the pale cream varieties. They are all perfectly self-coloured forms, and it is remarkable that the pale scarlet and

salmon pink, unlike most varieties with a deep yellow tinge, do not burn.

The other tinged forms described as nearly self-coloured, Blue pink tinged and King Edward tinged, have faintly tinged sap. A few yellow plastids have been noticed from time to time in the young flowers, especially in the standards, both in these two forms and in King Edward and Blue pink.

In all the bicoloured forms yellow plastids occur in large numbers: King Edward bicolor, the bicoloured pale Queen Alexandra, Blue pink bicolor, Helen Lewis, and the bicoloured pale cream, have only sap colour in the wings, but in the standard large clusters of golden yellow plastids are present as well as the sap colour. In the three pure recessive forms, deep Queen Alexandra, St George, and deep cream, not only is the sap more deeply tinged than in any of the others, but yellow plastids occur in large numbers in the standard and in smaller numbers in the wings.

It will be seen that the well-developed plastid colour corresponds to the deep yellow tinge, appearing in the standard only, except when in the presence of salmon sap it spreads also to the wings.

From the occurrence of so many forms in the offspring it is obvious that the deep yellow tinge in Queen Alexandra is complex and must be due to several coincident factors.

It is clear from microscopical observation that one factor concerned is a magenta factor affecting the sap. In its absence the ordinary colour factor (*R*)* makes the sap scarlet or salmon, while when the magenta factor is also present the sap is magenta; in other words magenta anthocyanin is epistatic to scarlet or salmon anthocyanin†. The pair of characters representing the presence and absence of this magenta factor we have designated *D*, *d*.

Another factor equally clear is that concerned in the production of bicoloured forms. Each self-coloured form has a corresponding bicolor, in which the standard appears markedly yellow owing to the presence of yellow plastids. The pair of characters involved here we have called *X*, *x*. In forms containing the dominant, *X*, the self-coloured forms, there are few or no yellow plastids present‡. In forms pure in *x* large numbers of yellow plastids occur in the standard. When the magenta sap factor is also absent yellow

* Bateson, Saunders, and Punnett, *loc. cit.*

† Cf. Wheldale, M., "The Colours and Pigments of Flowers, with Special Reference to Genetics," *Roy. Soc. Proc.*, B, Vol. LXXXI. 1909, p. 48.

‡ It is not easy from microscopical observation to make certain whether in the self-coloured forms white plastids always occur, corresponding to the yellow plastids of the bicolors, or whether in the self-coloured forms plastids are sometimes absent altogether.

plastids are found in the wings as well as in the standard, and the wings thus also take on a deep yellow tinge; but the standard has yet a deeper tinge and the forms are still bicoloured.

In order to produce all the forms which occur, another factor must be concerned. From the microscopical observations the exact nature of this factor is not clear. It appears to affect the whole flower and is mainly a sap tint; but some of the observations suggest that a small number of plastids is also concerned. As it is quite independent of both the other pairs of characters in the sense that the faint yellow tinge associated with the recessive character adds independently to the yellow tinge of the deepest forms, we have spoken of it in terms of this yellow tinge, leaving its nature an open question*.

Our three pairs of characters, then, are:

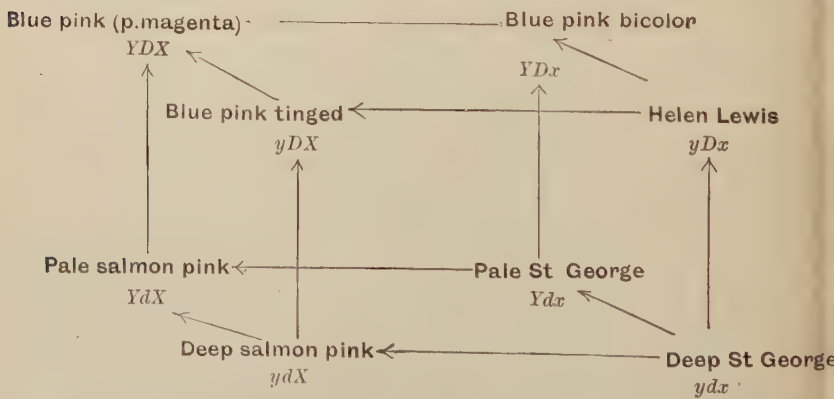
D, *d*, the presence and absence of a magenta factor affecting the sap throughout the flower, epistatic to salmon or scarlet;

Y, *y*, of which *Y* involves the non-appearance and *y* the appearance of a faint yellow tinge all over the flower;

X, white plastids (or no plastids), dominant to *x*, yellow plastids confined to or predominating in the standard.

Thus, speaking throughout in terms of the yellow tinge, it is the recessive member of each pair with which the yellow tinge is associated. The deepest yellow forms, deep Queen Alexandra, the deeper salmon, and deep cream, are those pure in all three recessive factors.

The relations between the various forms can be expressed diagrammatically thus, considering only the pink forms for the sake of simplicity.



* It may be important to note that in practice Blue pink bicolor is most easily distinguished from Helen Lewis bicolor in that it fades to an almost uniform and very pale pink, while Helen Lewis "burns" but does not fade. These two forms differ in the presence and absence of the faint yellow tinge. The paler St George

In Table I. is displayed our scheme based upon these three pairs of characters.

TABLE I.

Constitution of F_2 from Queen Alexandra × Dorothy Eckford.

Pinks				Reds		
Numbers		Description	Constitution	Description	Numbers	
found	expected				expected	found
17	14·3	Bl. pk.	*Y D X*	King Edw.	21·5 } 28·7	34
6	4·8	Bl. pk. tinged	*y D X*	K. Edw. tinged	7·2 }	
5	4·8	Bl. pk. bicol.	*Y D x*	K. Edw. bicol.	7·2	7
2	1·6	Helen Lewis	*y D x*	p. Qu. Alex. bicol.	2·4	
2	6·4 { 4·8	Salm. pk.	*Y d X*	p. Qu. Alex.	7·2 } 12·0	8
	6·4 { 1·6	d. salm. pk.	*y d X*	p. Qu. Alex.	2·4 }	
	{ 1·6	p. St George (salm. bicol.)	*Y d x*	d. (?) Qu. Alex.	2·4 }	
2	2·1 {				} 3·2	2
	{ 0·5	d. St George (d. sal. bicol.)	*y d x*	d. Qu. Alex.	0·8 }	
34	34				51·1	51

The scheme assumes that all three pairs of characters are simple Mendelian alternatives, the yellow tinge associated with each recessive character being visible by itself and adding independently to the intensity of the deeper yellow forms.

With regard to the bicolor tinge this independence is quite clear; but it might at first sight appear more reasonable to suppose the other two factors, both of which affect the whole flower, to be related in some way. For instance, one might hypothecate a *tinged* magenta factor, epistatic to salmon, magenta being epistatic to both. The proportions in F_2 afford no conclusive evidence for either hypothesis, as the numbers are too small; it is, however, rather striking that on the one which we have adopted, Table I., the experimental numbers show a marked deficiency among the yellower forms, and on the other quite as marked an excess. Owing to the delicacy often exhibited by these forms a deficiency among them might well be expected, but it would be

is probably to be distinguished in a similar way from deep St George. In at any rate a few cases pale St George was observed to fade (notably in Family 20, Table II.), but this fading was by no means as marked as in Blue pink bicolor. It appears that when plastid colour is associated with the faint yellow tinge (*xy*) it does not fade, but when plastid colour is associated with *Y* (*xY*) both sap and plastid colours fade.

difficult to give a reason for an excess. In the F_3 and F_4 families also, the proportion of salmon pink and salmon forms among the pinks and scarlet forms among the reds is consistently greater than the alternative theory would lead one to expect.

The facts as to the inheritance of the different forms do not give more certain aid: all the cases in which the inheritance should in theory distinguish between the two hypotheses are in practice of little use, as they necessitate separating from one another with precision forms which can only with difficulty be distinguished. It has, however, already been stated that, among the salmon pinks and the deep salmons, forms have from time to time been observed which were deeper than usual (deep salmon pink and deep St George), and their occurrence and their distinctness have led us to regard them as representing two additional forms. These forms fit easily into a scheme in which *y* and *d* are regarded as independently imparting a yellow tinge to the whole flower and as giving together a deeper tinge. Between the two forms of deep salmon, moreover, there is a difference in inheritance, the paler St George throwing pale cream, the deeper St George giving deep cream only.

Two families may be quoted here as examples of further detailed evidence which supports the view put forward. (*a*) A Blue pink tinged gave 14 Blue pink tinged : 3 Deep salmon pink. In this case it was quite clear that all the salmon pinks belonged to the deeper form, and it will be seen from the Table that when Blue pink tinged is pure in *X* the only pink form it should throw is the deeper salmon pink ($yDX : ydX :: 3 : 1$). (*b*) The offspring from a Blue pink bicolor included the paler St George and pale creams. The parent (*YDx*) was thus pure in *Y*, heterozygous only in *Dd* and colour. The numbers should accordingly be in the proportion of 9 : 3 : 4. The actual numbers were 30 : 7 : 12, the expectation 28 : 9 : 12. This family is strong evidence in support of the view that Blue pink bicolor and the paler St George differ in one character only (*D*, *d*) and thus that *d* is not merely an intensification factor.

III. *Details of F_3 and F_4.*

Table II. gives the numbers of the offspring in some of the families derived from F_2 and F_3 plants. Individuals belonging to all the forms respectively bred true, but the pure families are not given: unfortunately some of the largest families were pure and some of the mixed families very small.

Whites, etc. It is very difficult to separate out the pure whites from the various pale creams, and to attempt to give numbers from the families in F_3 and F_4 would serve no useful purpose. Deep cream always bred pure: the pale creams threw deep creams, and the whites both pale and deep creams.

Table II.

Offspring of the various forms occurring in F_2 and F_3.

Parent		*K.E.* and *K.E.t.*	*K.E.bi.*	*p.Q.A.*	*d.Q.A.*	*bl.pk.* and *bl.pk.t.*	*bl.pk.bi.*	*H.L.*	*p.s.pk.* and *d.s.pk.*	*p.StG.* and *d.StG.*	*wh.* and *p.cr.*	*d.cr.*
	1	19	6	3		6	13	2		3	12	
	2	15	4	5		9	5	1		1	12	
E.,	3	5	2		2		1		1	2	3	2
E.t.,	4	6	5		3						2	
or	5	10									3	
E.bi.	6	3	1			2	1			1		
	7	9	6		3							
	8		3			3	1					
	9		3		1							
	10			2				1	1	2	2	
	11			1	1				4	1	3	3
Q.A.	12			13[a]					4	4		
	13			11[a]					5	9		
	14			4					2			
Q.A....	15				12							3
.pk.	16					5	1	1	1		4	
or	17					9	5	4	10[b]	3		10
.pk.t.	18					3		1	4	2		
	19					14[c]			3[c]			
	20						30			7[d]	12	
	21						8	4			1	
bk.bi.	22						5	2				
	23						31				7	
	24						12				8	
H.L....	25							5		2		
s.pk.	26								8	3		
or	27								11	3		
s.pk.	28								21	10		
	29								35	18		
StG.	30									3		1
or	31									5		5
StG.	32									7	2	
	33									3	3	

[a] Mixed *p.* and *d.Q.A.*
[b] 6 *p.s.p.* and 4 *d.s.p.*
[c] *b.p.t.* and *d.s.p.*
[d] *p.StG.*

St George bicolors (deep St George = *yyddxx*; pale St George = *YY* or *Yyddxx*). One of the F_2 St Georges bred true (12 plants), and the other did not set seed. Seeds were sown from four of the individuals found in other families in F_3, and of these families (30—33, Table II.) two contained deep creams and two pale creams, the pale creams showing a marked difference between wings and standard. The parents of the two former families were

certainly of the deeper kind, deep St George, those of the two latter probably pale St George.

Salmon pink self-colour ($\text{deep salmon pink} = yyddX\frac{X}{x}$; $\text{pale salmon pink} = Y\frac{Y}{y}ddX\frac{X}{x}$). Unfortunately all the families derived from plants with salmon pink flowers were pure as to pink colour, containing no creams. As would be expected from the scheme, no other pink forms except the two kinds of deep salmon were given. Two small families (26 and 27, probably from deep salmon pink parents) gave salmon pinks : deep St George :: 3 : 1; in one of these the seeds from two of the salmon pink offspring were sown, one was pure, the other gave deep St George again 3 : 1.

The other two larger families (28 and 29) gave St Georges in the ratio of 2 : 1. In Family 28 it is recorded that the St Georges were pale; in Family 29 both kinds of salmon pink and both kinds of St George (deep and pale) were recorded, though it is not possible to estimate the actual number of each. It may be that some of the deep salmon pink forms have been mistaken for pale St George, which would bring the proportion nearer to 9 : 7; or, more probably, the deficiency of salmon pinks is to be compared with a similar deficiency in F_2 and is due to some other cause.

Helen Lewis bicolor ($yyD\frac{D}{d}xx$). All the Helen Lewis plants of which seed was sown bred pure except one, from which a small family (25, Table II.) containing deep salmons was obtained. As Helen Lewis can only be heterozygous in *D*, deep St George is the only form to be expected (apart, of course, from creams).

Blue pink bicolor ($Y\frac{Y}{y}D\frac{D}{d}xx$). According to the scheme it should be possible for Blue pink bicolor to throw all the bicoloured forms, viz. Helen Lewis and both kinds of deep salmon. The parent of Family 20 (Table II.) is apparently heterozygous in *D*, giving the paler St George along with pale cream. In other cases (21 and 22) it is heterozygous in *Y*, giving Helen Lewis. The two families throwing only pale creams taken together give a 3 : 1 proportion.

Blue pink and *Blue pink tinged, self-colours* ($bp = Y\frac{Y}{y}D\frac{D}{d}X\frac{X}{x}$; $bpt = yyD\frac{D}{d}X\frac{X}{x}$). It is exceedingly difficult to distinguish, certainly, between these two forms. Blue pink tinged should give Helen Lewis, deep salmon pink, deep St George, and pale and deep creams. In one case, a small family, all three possible pink forms occurred (Family 18). In two other small families salmon

pink and deep salmon occurred, but no Helen Lewis; probably the absence of Helen Lewis was accidental. One family, of which the parent was certainly blue pink tinged, was pure in X and heterozygous in D only, giving the deep form of salmon pink (Family 19).

Deep Queen Alexandra ($yyddxx$). This was always pure as to its deep yellow tinge. Two large pure families were obtained, and two others which gave deep cream. Unfortunately no family occurred which contained deep St George, the other form to be expected.

Pale Queen Alexandra $\left(yyD\frac{D}{d}xx;\ Y\frac{Y}{y}ddX\frac{X}{x};\ yyddX\frac{X}{x};\ Y\frac{Y}{y}ddxx\right)$. Of the four forms, that of which the constitution is given last has probably been classified as deep Queen Alexandra: it would be expected to give the two forms of St George, and, by analogy with pale St George, pale cream as well as deep cream, but no family of this type occurred among the few grown. The first form should give Helen Lewis and deep St George. Family 10 was probably derived from a parent of this type, as it contained an undoubted Helen Lewis which bred pure; though the presence of the salmon pink is unexpected. The second and third forms could give salmon pink and deep salmon but no Helen Lewis (Families 12 and 13). These are the self-coloured forms, and several families were obtained which were pure in X giving only salmon pink.

King Edward $\left(Y\frac{Y}{y}D\frac{D}{d}X\frac{X}{x}\right)$; *King Edward tinged* $\left(yyD\frac{D}{d}X\frac{X}{x}\right)$; *King Edward bicolor* $\left(Y\frac{Y}{y}D\frac{D}{d}xx\right)$. These forms are not easily distinguished apart from their inheritance. King Edward could, of course, give all the forms, red, pink, and white; from King Edward bicolor, on the other hand, only the bicoloured forms would be expected. One family of 22 plants derived from a King Edward bicolor, but not mentioned in the Table, consisted of three or four forms, which could not be disentangled; they were probably King Edward bicolor, the two bicoloured pale Queen Alexandra, and deep Queen Alexandra. The other families do not call for special remark.

IV. *General conclusions from the study of the F_3 and F_4 generations.*

On the whole the behaviour of the F_3 and F_4 families, derived from self-fertilised plants in F_2, supports the scheme already outlined.

The first outstanding fact is that the forms are readily arranged into two series, consisting respectively of almost self-

coloured and markedly bicoloured forms. Forms belonging to the self-coloured series can throw those in the bicoloured series, but the reverse has never been known to happen.

The arrangement into pairs of corresponding forms, one self-coloured and one bicoloured, which was suggested by their appearance, is found to be supported by the correspondence in the inheritance of the members of each pair. Thus Blue pink gives all the pink forms, self-coloured and bicoloured; Blue pink bicolor gives all the bicoloured forms. Similarly Salmon pink gives only Salmon pink and St George; St George gives no other pink form. The two forms in each case differ from each other in that the second is pure in the recessive bicolour factor which is found to be associated with the presence of yellow plastids in the standard (*xx*), whereas the first carries the corresponding dominant character, so that it may be heterozygous (*Xx*).

The inheritance of the red and pink forms points to correspondences between them similar to those suggested by their appearance. For instance, it appears that tinged King Edward is the red form corresponding to Blue pink tinged, since the latter is constantly found in families derived from tinged King Edward, but has never occurred in a family derived from pale Queen Alexandra; also that the bicoloured pale Queen Alexandra is the intense form of Helen Lewis, since Helen Lewis is found in a family derived from a pale Queen Alexandra parent, but has never occurred in families derived from King Edward *X*.

As is suggested by microscopical observation, deeply tinged sap as well as yellow plastids is necessary in order to produce deep cream. Deep cream never occurs in families derived from pale Queen Alexandra unless deep Queen Alexandra or the deeper St George appear in addition to the sap-coloured forms among the offspring. Thus only deep Queen Alexandra and the deeper St George correspond to deep cream.

There is one remarkable family which stands out from the rest as an exception to the general agreement with our scheme. It (Family 17) was derived from a blue pink parent which had been recorded as distinctly tinged. It included all the pink forms except unquestionable Blue pinks, but gave neither whites nor pale creams. The pinks stood to the deep creams in the ratio of 3 : 1. Not only is the absence of white and pale cream forms remarkable, but the presence of Blue pink bicolor is unexpected and the proportion of deeply yellow-tinged forms is altogether peculiarly high. Of the ten salmon pink forms, four were of the deeper kind. No explanation of this aberrant family can be attempted, but it is hoped that further evidence may be forthcoming to throw some light upon it.

Other Work on the Yellow Tinge in Sweet Peas.

Varieties tinged with yellow have hitherto been little used in Mendelian experiments. It appeared early in Mr Bateson and Miss Saunders' work on sweet peas* that cream was recessive to white in both sap-coloured and non-sap-coloured forms; but the results of only two crosses involving cream are given.

In Queen Victoria × Emily Henderson the ratio of non-yellow-tinged forms to yellow-tinged forms is about 1·5 : 1. Queen Victoria was a very pale pink deeply tinged with yellow, and its constitution with regard to yellow may have resembled that of our deep salmon forms. The proportion is very suggestive of that to be expected on a scheme founded on three pairs of characters as illustrated by our pinks: Blue pink tinged and Blue pink would certainly have been counted together as "not cream," and the others as "cream," giving a proportion of 19 : 15 out of 34 (see Table I.).

In another cross, Venus × Emily Henderson, non-cream behaved as a simple Mendelian dominant to cream: probably Venus had only one of the possible cream characters.

Summary.

1. The deep yellow tinge in deep Queen Alexandra, deep salmon (St George) and deep cream sweet pea flowers appears to be dependent on three coincident recessive characters.

2. Each recessive character brings in a component which is visible by itself on the magenta or pink ground, and adds independently to the intensity of the deeper forms. Two of the factors tinge the whole flower, the third chiefly affects the standard producing marked bicoloured forms.

3. Microscopical examination shows that one of the factors imparting a tinge to the whole flower, producing self-coloured forms, affects the sap only, tinging it deeply. The other similarly imparts to the sap a tinge which, however, is fainter and is also commonly associated with a few yellow plastids. The third factor, which chiefly affects the standard, is connected with the occurrence of large clusters of golden yellow plastids in the cells.

* Bateson, W., Saunders, E. R., and Punnett, R. C., *Reports to the Evolution Committee of the Royal Society*, No. II., 1905, pp. 85—88 and 94—95.

4. Thus deep or pale magenta sap colour is epistatic to scarlet or salmon sap colour. In addition, corresponding to another pair of characters, the magenta sap may be pure magenta or magenta tinged with yellow, and the salmon sap either pale or deep salmon. Finally, whatever the sap colour, the absence of yellow plastids is dominant to the occurrence of yellow plastids.

5. There are thus between deep or pale magenta and deep scarlet or salmon a number of forms intermediate in yellowness. These may be collected into two categories, self-coloured and bicoloured.

6. Each self-coloured form has a corresponding bicoloured form to which it is dominant, so that the forms may also be arranged in pairs. The difference between the members of a pair is that the self-coloured form has no yellow plastids, while the bicoloured form has numerous yellow plastids in its standard.

7. Unless the flower has yellow plastid colour it does not "burn." The two most deeply tinged self-coloured forms, pale scarlet and salmon pink, remain quite sun-proof.

8. Only the forms with both a deep tinge in the sap and yellow plastid colour throw deep cream without pale cream, but the relations of the white and cream forms to the pinks are still not quite clear; in one anomalous family containing all grades of pinks all the uncoloured forms were deep cream.

9. The red forms taken together stand to the pinks approximately in the ratio of 9 : 7. It therefore appears that two factors are necessary to produce the intensification by which pink becomes red.

Colloidal form of Nastvogel's Osazone. By H. J. H. Fenton, Sc.D., F.R.S., Christ's College, and W. A. R. Wilks, B.A., Gonville and Caius College.

[*Read* 28 November 1910.]

By the action of phenylhydrazine on dibromopyruvic acid, Nastvogel, in 1887, obtained the compound

$$CH(N_2HPh)\cdot C(N_2HPh)\cdot COOH$$

which he regarded as the "dihydrazone of glyoxal-carboxylic acid"; evidently it also represents the osazone of hydroxypyruvic acid or of tartronic semi-aldehyde. Subsequently it has been shown that the same compound results from the action of phenylhydrazine on (1) the so-called hydroxypyruvic acid from collodion wool*; (2) the products of oxidation of glyceric acid or oxalacetic acid† and (3) on mesoxalic semi-aldehyde‡.

This osazone crystallises in beautiful orange-yellow prisms which are nearly insoluble in water but which dissolve easily in organic solvents or in alkalis. The same product may be obtained by boiling the phenylhydrazine salt of dihydroxymaleic acid with water§, but, under these conditions, the osazone remains, for the most part, in solution and the filtered liquid has all the characters of a colloidal solution. It is readily coagulated by minute quantities of electrolytes and, in an electric field, it moves to the anode. With electro-negative colloids, such as arsenious sulphide, it is not precipitated; but with colloidal ferric hydroxide, a dark brown precipitate is obtained from which the osazone can scarcely be extracted by organic solvents. In its general characters therefore the solution behaves as a negative colloid of the suspensoid class.

With metallic salts, the order of coagulative powers is in the direction indicated by Schultze's rule, being greatest for trivalent and least for univalent kations. But the behaviour of acids is quite exceptional.

It is now very generally recognised that the degree of ionisation of the electrolyte and the speed of the reactive ion are factors of importance in determining the coagulative power of an electrolyte‖,

* *Will. Ber.* 1891, 24, 400.

† Fenton and Jones, *Trans. Chem. Soc.*, 1900, 72, and 1901, 98.

‡ Fenton and Ryffel, *ibid.* 1902, 426.

§ Fenton, *loc. cit.*, 1905, 809.

‖ Compare, for example, Spring, *Rec. Trav. Chim.*, 1900 (19), 204, and Freundlich, *Zeit. Physikal. Chem.* 1903 (44), 129.

but these factors usually appear to be of secondary importance in comparison with the valency of the reactive ion. Thus, although acids are more reactive than their salts with univalent metals, the coagulative powers are much of the same order. Freundlich, for example, found, for the quantities necessary to coagulate arsenious sulphide, the relative numbers

$NaCl$	NH_4Cl	HCl	$\frac{H_2SO_4}{2}$	$BaCl_2$	$AlCl_3$
71·2	59·1	42·9	42	0·96	0·13

and Picton and Linder found, for sulphates,

Na	NH_4	H	Ca	Al
1110	778	750	26	0·6

In the present case the sensitiveness to hydrogen ions appears to be extraordinarily great; a solution of the osazone which is coagulated, for example, by a single drop of decinormal hydrochloric acid is unaffected, under similar conditions, by several drops of five times normal sodium chloride. A rough quantitative measurement indicated that the hydrogen ion is about 300 times as effective as the sodium ion. Even carbon dioxide when passed into the solution brings about immediate coagulation.

The only explanation of this abnormality which suggests itself to the authors, is that a minute quantity of some basic substance (e.g. phenylhydrazine, resulting from hydrolysis of the original salt or aniline, from the oxidising action of phenylhydrazine in the osazone formation) may be present in the solution and may exert a "protective" influence which is removed on neutralisation by the acid.

Notes on Protein Hydrolysis. By F. W. Foreman, B.A., F.I.C., Gonville and Caius College. (Communicated by Professor Wood.)

[*Read* 14 November 1910.]

Every farmer must feed a considerable number of animals on his farm. For this purpose he grows certain foods—hay, straw, roots, etc. These are for the most part rich in carbohydrates, and relatively deficient in fat and protein. Hence the farmer finds it necessary to purchase concentrated feeding stuffs rich in fat and protein, in order to supplement his home grown foods. The proteins of many foods have been separated and hydrolysed, and their composition is very variable. It appears reasonable that a considerable economy in protein might be effected by purchasing feeding stuffs whose proteins were known to be rich in the groups in which the proteins of home grown foods are deficient. Before this ideal can be attained, it is necessary that the proteins of many more common feeding stuffs should be separated and hydrolysed. It was with this object that the hydrolysis of the protein of linseed was undertaken.

The crude protein of linseed was separated by solution in 0·2 per cent. potassium hydrate, from which it was precipitated by acidifying. After washing with water, alcohol, and ether, and drying, the protein was hydrolysed by boiling with hydrochloric acid in the usual way. The products of hydrolysis were separated by Fischer's methods, when the following results were obtained.

	Per cent.
Glycine	present
Alanine	1·03
Valine	12·71
Leucine and Isoleucine	3·97
Proline	2·85
Phenyl alanine	4·14
Aspartic acid	1·65
Glutaminic acid	11·58
Serine	present
Tyrosine	0·65
Arginine	6·06
Histidine	1·66
Lysine	1·19
Ammonia	1·94
Tryptophane	present
	49·43

During the investigation several points of general interest have been noted.

1. It was found possible to separate practically the whole of the glutaminic acid as the hydrochloride by the following

procedure. The acid solution resulting from hydrolysis was cooled in ice and saturated with hydrochloric acid in the usual way. It was then kept in an ice chest and from time to time cooled in a freezing mixture until no more crystals separated. This treatment was continued for 9 days, when 11·4 per cent. of glutaminic acid was separated and only 0·2 per cent. subsequently found.

2. The percentage of valine is very high, 12·7 per cent. No other protein, so far as the author is aware, has been shown to yield more than 2 per cent. The valine was separated from leucine by the method of Levene* and van Slyke. It appears probable that many valine and leucine figures will be found to need revision when this method has been more widely applied.

3. The percentage of tyrosine in linseed protein appears to be very low. It is noteworthy however that determinations of tyrosine in the same protein by different workers often differ very widely. From this it may be concluded that the usual method of separating tyrosine by crystallisation is unsatisfactory.

In attempting to prepare lead salts from a mixture of amino-acids resulting from hydrolysis of casein, the author obtained a precipitate which proved to be a basic lead salt of tyrosine. This precipitate was obtained in three fractions, the first by addition of basic lead acetate to a faintly ammoniacal solution, the second by further addition of ammonia, the third by addition of much alcohol. On removing the lead from each fraction by sulphuretted hydrogen, practically pure tyrosine crystals were obtained.

A further quantity was made by adding basic lead acetate to a faintly ammoniacal solution of pure tyrosine. 1·1973 gms. pure tyrosine was dissolved in the least possible quantity of water containing 1·5 c.c. strong ammonia. Saturated basic lead acetate solution was added slowly to the hot liquid as long as any precipitate was obtained. The flocculent precipitate was at once filtered, washed with alcohol, and finally with ether, and dried.

On analysis the substance was found to contain 2·44 per cent. N, and 61·98 per cent. Pb. These figures correspond to the formula $2Pb(C_9H_{10}NO_3)_2 . 5Pb(OH)_2$, which should contain 2·39 per cent. N, and 61·95 per cent. Pb.

From the mother liquor, further small amounts of lead salt separated on cooling and on addition of alcohol. The total weight of lead salt obtained was 3·251 gms., containing ·0803 gm. N. The original tyrosine contained 7·70 per cent. N, = ·0922 gm. N. Hence 87 per cent. of the N of the tyrosine was recovered in the basic lead salt. This subject is being further investigated in the hope that it may provide a more satisfactory method of estimating tyrosine in products of hydrolysis.

* *Journal of Biological Chemistry*, vol. VI. 1909, p. 391.

The Discharge of positive electricity from Sodium Phosphate heated in different gases. By Frank Horton, M.A., St John's College.

[*Read* 28 November 1910.]

As the result of a recent spectroscopic investigation of the products formed when an electric discharge is sent from aluminium phosphate heated in a vacuum to a surrounding electrode, the author came to the conclusion that the carriers of positive electricity from that salt were molecules of carbon monoxide gas*. This conclusion was based on the facts that carbon monoxide gas was always produced in the apparatus, and that its molecular mass corresponds with that required by the determinations of $\frac{e}{m}$ for the carriers of positive electricity from various solids when heated.

The number of substances upon which experiments have been made has quite recently been largely increased by Richardson and Hulbirt†, who have used materials of widely differing properties and atomic weights and find that the value of $\frac{e}{m}$ for the positive ions is in all cases about the same as that first found by Sir J. J. Thomson, when experimenting with an iron wire heated in a vacuum. Assuming that the charge e is the same as that carried by the hydrogen atom in electrolysis, the mean value of m determined by Richardson and Hulbirt from observations with 15 substances is 25·3, a number which, considering the difficulties of the experiments, is in good agreement with the molecular weight of carbon monoxide (27·9).

Richardson holds a different view of the nature of these ions. He considers that they are atoms of sodium arising from impurities present in the substances used as the anodes in the various experiments. He states‡: "It is probable that traces of carbon monoxide are always present when a metal is heated in a vacuum in the kind of apparatus used in the present experiments, but it is difficult to see why practically all the ionization should be due to this gas in the case of all the substances investigated." In the paper already referred to, the author has pointed out that it is not necessary for the carbon monoxide to be produced in the first instance from the heated anode. If it is present in the apparatus,

* *Proc. Roy. Soc.*, A. vol. lxxxiv. 1910.
† *Phil. Mag.*, vi. vol. xx. p. 545, 1910.
‡ *Phil. Mag.*, vi. vol. xx. p. 558, 1910.

it may act as the positive ion, for the spectroscope gives ample evidence that in vacuum tubes at low pressures the positive ion is usually CO, the spectrum of which often masks that of other gases which are known to be present. It was thought desirable to test whether the positive leak from a glowing solid was greater in carbon monoxide than in air or other gases, as would be expected if it acts as the positive ion.

In the experiments with aluminium phosphate, the positive leak was thought to be due to the phosphorus contained by the salt, which in this compound can be raised to a high temperature. With a view to seeing whether this were so, experiments are being made to compare the positive leak from different phosphates under similar conditions. Sodium phosphate was used in the experiments described in this paper, which were conducted in the following manner.

The anode consists of a strip of platinum foil about 2 cms. long and 3 mm. wide, which can be heated by means of an electric current. Its temperature can be obtained by a thermocouple consisting of two fine wires of platinum and platinum-rhodium fused together at one end, the junction being just welded on to the centre of one side of the platinum strip. Before being finally placed in the apparatus, the platinum strip was very carefully cleaned by boiling in nitric acid and heating in air, and then covered with a layer of sodium phosphate by evaporating a water solution of that salt upon it. When in position the strip was situated vertically in a discharge tube between two parallel platinum plates which together formed the negative electrode. These plates were each about three times the area of the strip and were placed about one centimetre apart at equal distances on either side of it. The whole apparatus was most carefully cleaned out with hot chromic and nitric acids before the strip was finally placed in position. There was no wax or grease in the discharge tube; the platinum strip fitted into position with a well-made ground glass joint having a mercury seal. This apparatus was connected to a mercury pump and McLeod gauge through a phosphorus pentoxide drying bulb. Different gases could be introduced into the pump through glass stop-cocks after drying over phosphorus pentoxide. The gases used in the present experiments were air, oxygen, carbon monoxide, and hydrogen.

After fitting the anode into position in the discharge tube, the gas pressure in the apparatus was reduced to about ·05 mm. of mercury, and preliminary observations were made to decide upon a suitable temperature at which to make comparisons of the thermionic currents in different gases. These currents were measured by means of a Nalder galvanometer giving a deflexion of 1 scale division for a current of $7{\cdot}99 \times 10^{-10}$ ampere. This

could be shunted for measuring larger currents. With the pressure ·05 mm. it was found that a current could be detected when the anode was heated to about 400° C. The current then increased rapidly with the temperature in the exponential manner which has been found to hold for the positive leak from other substances.

As is usually the case for the positive leak from heated substances, it was found that on first heating, if the temperature was kept steady, the current rapidly decreased with time. When it had attained a fairly steady value, it was thought desirable to rid the apparatus as completely as possible of traces of carbon monoxide gas by gently heating the glass walls and repeatedly washing out with pure dry oxygen. The oxygen used was prepared by the electrolysis of a strong solution of pure barium hydrate in distilled water, and was dried over phosphorus pentoxide for about 16 hours before being introduced into the apparatus.

On testing the positive leak in oxygen, it was found to be of about the same magnitude as that in air at the same temperature and pressure. It still decreased with time, but at a slower rate than at first. A series of observations of the leak under different potential differences was made with the anode at various temperatures. This was done with both increasing and decreasing voltages in order to eliminate the time effect. The results obtained were similar to those given by Richardson* for platinum, and showed that the potential difference required for saturation at any given pressure depends on the temperature of the anode. For instance, with a pressure of about ·2 mm. of oxygen, it was found that a saturation current could be obtained with 10 volts at 720° C. At 850° C. 24 volts were needed, while at 920° C. 40 volts were required to saturate.

The behaviour in oxygen was sometimes irregular. On one occasion this gas was left in the apparatus at a pressure of ·184 mm. overnight. The next morning the gas pressure had decreased to ·177 mm., and the saturation current at 700° C. began at about 10 times the value it had the night before. However, it decreased rapidly and in about 10 minutes was steady at about one-half the value which it had on the previous evening. The pressure meanwhile had risen to ·180 mm., which seems to show that oxygen had been absorbed by the anode during the night and driven out again on heating, and that the increased leak obtained was probably due to this cause.

When the positive leak in oxygen had become fairly steady, a series of observations of the saturation current with the anode at 800° C. was taken at different pressures, for comparison with similar series for other gases. At this temperature a potential difference of 40 volts was found to produce saturation at all the

* *Phil. Trans.*, A. vol. ccvii. p. 8.

pressures used in these experiments. 800° C. was chosen as the standard temperature for these comparisons for the following reasons:

(1) The thermionic current at this temperature is large enough to be measured accurately.

(2) The gradual diminution of the current with time (which was still going on, though slowly) is much less rapid at this temperature than at higher temperatures.

(3) In making a long series of observations, it is best to work at as low a temperature as possible, because at high temperatures the platinum strip becomes gradually thinner by sputtering, and this usually takes place in such a way as to spoil the uniformity of the electrical resistance of the strip, so that after a time the thermo-junction may no longer be at the hottest point, and in adjusting the thermo-electric current to the same value, the temperature of other parts of the strip may be much higher. As the thermionic current increases so rapidly with the temperature, this would entirely vitiate the results obtained. In working with lime-covered platinum cathodes, the author found that reliable comparisons of the kind to be effected here could only be obtained by working as rapidly as possible, and by using temperatures which were not too high.

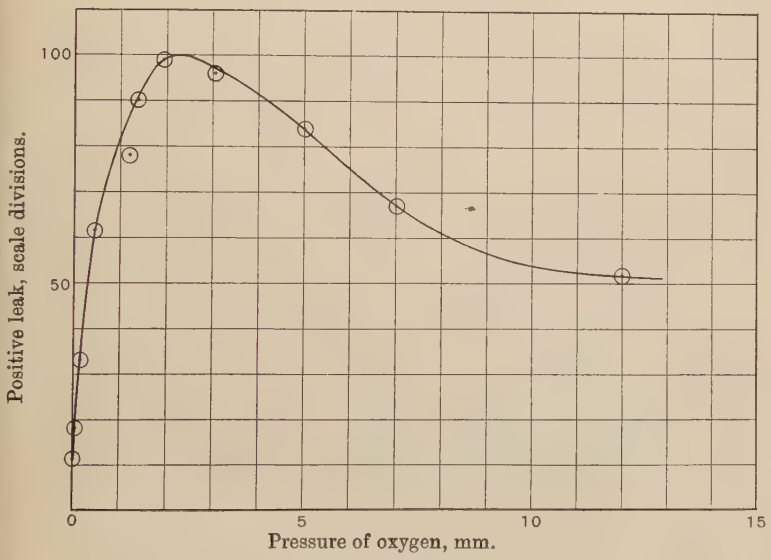
In the series of observations at the standard temperature in different gases, the results of which are about to be given, the thermionic current at the highest pressure was first observed. When this had been at a steady value for a few minutes, the heating current was cut off from the anode, and the gas pressure in the apparatus was reduced. The anode was then raised to 800° C., and the positive leak again measured when it became steady—usually in the course of a minute or two. These operations were repeated until the pressure had been gradually reduced to a very low value. It should be mentioned that, if the temperature had been inadvertently raised too high (above 800° C.), the leak at 800° C. was, at first, greater than the normal value and took some time to fall to the steady condition. An effect of this nature has been observed by Richardson* with the positive leak from platinum in oxygen. He attributes it to the warming of the walls of the discharge tube, but I do not think it is due to that cause.

The positive leak in oxygen.

The observations of the saturation current in oxygen gas at gradually diminishing pressures have been plotted against the

* *Loc. cit.*, pp. 13 and 21.

corresponding pressures in Curve I. It will be seen that, as the pressure is reduced, the thermionic current rises to a maximum value at between 2 and 3 mm. pressure, after which it decreases very rapidly. When the observation at the lowest pressure had been taken, more oxygen was admitted to a pressure of about ·5 mm., and the positive leak was found to increase to the value it had at this pressure, when the pressure was being gradually reduced. There was a slight tendency for this leak to increase with time, but the fact that it was the same as before shows that the leak in oxygen had become fairly steady, and that the variation



Curve I.

of the current with the pressure of the gas is accurately represented by the curve.

The appearance of this curve at first seems to suggest that ionisation by collisions is coming in. It is very similar in form to that obtained by H. A. Wilson* for the negative leak from hot platinum in air under a potential difference of 250 volts. That curve is completely explained by Wilson on the assumptions that the rate of evolution of negative ions from the surface of the platinum is independent of the gas pressure, and that these ions produce others by collisions with the gas molecules when moving under the influence of the large electric intensity used in the experiment. An explanation on similar lines cannot be applied

* *Phil. Trans.*, A. vol. ccii. p. 254, 1903.

to the case of the positive leak in oxygen, for we are here dealing with the large positive ions, and moreover the electrical force used was very small, the current-electromotive force curves having shown that at all the pressures at which observations were made the saturation current was attained with 40 volts.

In a recent paper on the positive leak from heated aluminium phosphate, Garrett* gives curves connecting the current and gas pressure, which are of similar shape to Curve I. He finds that the pressure of maximum leak is greater the lower the temperature of the anode, but from his curves it would appear that with the anode at 800° C., the maximum leak in air or in carbonic acid gas would be obtained at a pressure of between 20 and 30 mm. Garrett explains the peculiar manner in which the current varies with the pressure, by supposing that neutral doublets are driven off when the salt is heated, and that the current is due to the breaking up of these doublets on collision with the gaseous molecules.

In the experiments described in the present paper, no current could be detected by the galvanometer when the heated phosphate was charged negatively, and this forms a serious objection to the doublet theory, for we should not expect the expulsion of neutral doublets to be controlled by the direction of the electric field. Garrett was able to detect a small negative leak, but he was working at much higher temperatures than that used in the present investigations. He was also able to detect the presence of neutral doublets, but the number of these ejected from the hot salt would appear to be insufficient to account for the large increase in the thermionic current at certain pressures.

The positive leak in carbon monoxide.

After the experiments with oxygen, the apparatus was pumped out as completely as possible and carbon monoxide gas was admitted. This gas was prepared by heating pure crystallised potassium ferrocyanide with pure sulphuric acid. It was dried over phosphorus pentoxide before being admitted to the apparatus. The saturation current with the anode at 800° C. was at first larger than the leak in oxygen under the same conditions. It rapidly increased with time, as may be seen from the following figures:

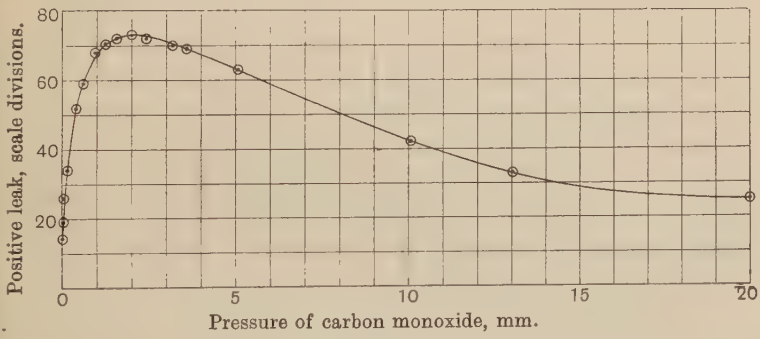
Time	5.28	5.30	5.33	5.35	5.37
Galvanometer deflexions	242	270	356	393	426

The shunt of the galvanometer had then to be altered. When this had been done, it was found that the leak had become steady.

* *Phil. Mag.*, VI. vol. XX. p. 573, 1910.

A series of observations at different pressures was therefore at once taken. Each observation took a minute or two, and the currents were found to be steady over this interval of time. The current-pressure curve obtained was similar in form to Curve II, which represents the result of a second series of observations taken over a rather larger range of pressure. On the day following the first series of observations, it was found that the positive leak at the lowest pressure of the night before had decreased somewhat and there was a slight tendency to decrease with time.

More dry carbon monoxide was admitted to the apparatus to a pressure of about 23 mm., and the observations at gradually diminishing pressures were repeated. On first testing the leak at 23 mm. pressure it was found to increase slowly with time —from 18 to 32 scale divisions in 19 minutes. After this it was fairly steady, and remained so during the short time of each of the succeeding observations. In Curve II, the galvanometer deflexions are plotted against the corresponding pressures. This curve is of the same type as that obtained with oxygen, and shows a pressure of maximum leak at about 2 mm.



Curve II.

With the anode at 800° C., in carbon monoxide gas, it was found that the thermionic current was saturated

with 20 volts at a pressure of ·06 mm.,
with 30 volts at a pressure of 3·5 mm.,
with 40 volts at a pressure of 20 mm.

No negative leak could be detected by the galvanometer with 160 volts P.D., even when the phosphate was heated to 900° C. at a low pressure.

The positive leak in hydrogen.

The apparatus was next pumped out as completely as possible, and then washed out by repeated fillings with pure dry oxygen.

The positive leak in this gas was again tested before filling the apparatus with hydrogen. With oxygen at a pressure of 8 mm., the temperature of the anode was adjusted to 800° C. The thermionic current commenced at a much smaller value than it had in this gas when tested before the observations in carbon monoxide, and it decreased as time went on. This will be seen from the following figures:

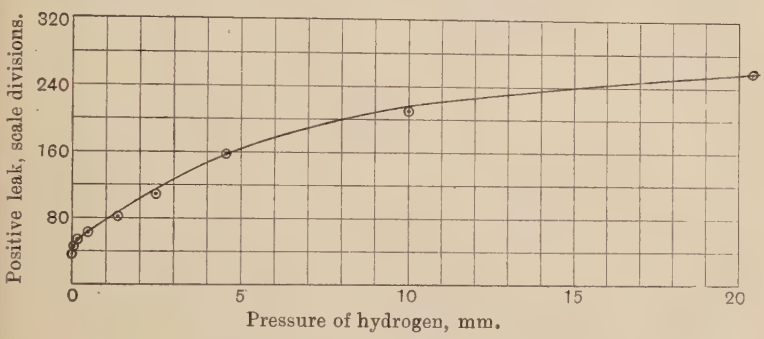
Time	3.23	3.26	3.32	3.36	3.37	3.39	3.41	3.46	3.49	3.52
Galvanometer deflexions	68	54	53	43	40	38	40	35	32	32

Observations at two or three pressures were taken in oxygen after the leak had become steady. After leaving the apparatus overnight at a low pressure, the same value of the current was obtained at this pressure on the following day. The anode was therefore taken as being in a steady state. The remaining oxygen was pumped out as completely as possible, and pure dry hydrogen was admitted. At once a much larger positive leak than had yet been measured was obtained. This was fairly steady for a few minutes, and so a series of observations at different pressures was at once taken. The leak was found to diminish gradually with the pressure, as that was reduced from 8 mm. to 0·005 mm. There was no sign of a maximum current at 2 or 3 mm. pressure, as was obtained with oxygen and with carbon monoxide. It was thought that this might perhaps be due to a decrease in the current with time, although the leak at each pressure seemed fairly steady. The pressure was therefore finally increased to 1·4 mm., and it was found that the thermionic current was now of the same value as at this pressure when the pressure was being reduced, so that it seems that the gradual decrease with the pressure is a genuine effect.

On testing the leak on the following day at this pressure it was found to be a little larger (49 scale divisions instead of 43), but on taking a series of observations of the variation of the leak with time, it was found to fall off gradually to about $\frac{1}{2}$ value in 30 minutes. At the same time the gas pressure in the apparatus decreased from 1·428 mm. to 1·404 mm., but the decrease in the positive leak was much more than could be accounted for by this slight decrease in the pressure.

More hydrogen gas to a pressure of 20 mm. was then passed into the apparatus. With the anode at 800° C. the thermionic current was the same as the steady current finally obtained at the lower pressure of 1·4 mm., referred to above. However, it was not steady at this value, but was decreasing rapidly. It continued to decrease for about an hour when it became fairly steady at about $\frac{1}{3}$ of the value first obtained. Experiments showed that the P.D. of 40 volts used saturated the current at this pressure.

Another set of observations at decreasing pressures was then taken and the results of these are plotted in the accompanying Curve III, which is similar to that given by the first series of observations with hydrogen. From this curve it will be seen that between 20 mm. pressure and a high vacuum there is no sign of the positive leak going through a maximum value.



Curve III.

After these observations the pressure of hydrogen was again increased and another similar curve was obtained, but the leak at each pressure was now somewhat less than that shown in Curve III. When the pressure was increased from ·008 mm. to 12 mm., for the purpose of taking these observations, the positive leak began at 125 scale divisions. In about 5 minutes it had *increased* to 136 divisions, and was then fairly steady. The apparatus was left at this pressure overnight, and on testing on the following day the current began at 128 scale divisions, and slowly increased in the course of half an hour to 146 divisions, at which it remained constant for several minutes. The series of observations at gradually diminishing pressures was then taken. At each pressure the current was fairly steady, but it was sometimes found that the leak would suddenly increase to double or treble its normal value, and then slowly return to the value it had before the disturbance. I think these disturbances are due to a sudden evolution of ionised gas from inside the anode caused by a crack appearing on its surface. Richardson noticed that the surface of a platinum wire becomes pitted and cracked after heating for a long time in hydrogen, but this effect was not produced by heating in oxygen.

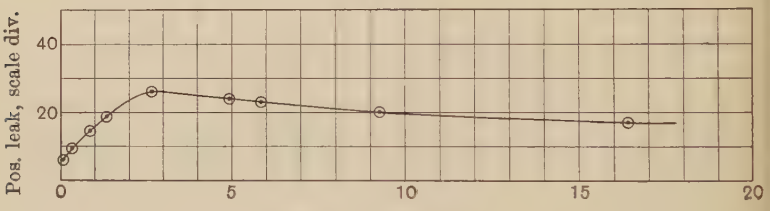
It is well known that the presence of hydrogen greatly increases the negative leak from heated solids, but even in this gas with the platinum strip at 800° C. I was unable to detect any negative leak with the Nalder galvanometer.

Further observations of the positive leak in oxygen.

When the experiments with hydrogen were completed, the gas was pumped out of the apparatus, and oxygen was admitted to a pressure of about 16·5 mm. The leak in oxygen was smaller than before, and much smaller than the leak in hydrogen. It decreased rapidly when the anode was kept at 800° C. for some time; the decrease in the first half hour will be seen from the following numbers:

Time	3.40	3.47	3.53	3.56	3.58	4.3	4.5
Galvanometer deflexions	33	29	25	22	20	18	17

When the current had become fairly steady, observations at various pressures were again taken. The results of these are plotted in Curve IV. It will be seen that the leak still had a maximum value at between 2 and 3 mm. pressure, though the increase is not nearly so marked as in earlier observations with this gas.



Curve IV.

On the following day the observations were repeated and a similar curve obtained, but the current at each pressure was now only about one-half the corresponding value from Curve IV. The leak, however, now seemed to be quite constant, and on increasing the pressure again, and repeating the observations, the same values of the current were obtained. On leaving the apparatus for a day and then retesting, the leak was still found to be steady at about the same value.

Summary of the different results.

The following table contains the saturation thermionic currents at various pressures of the different gases used, in the order in which the observations were taken. The values at each pressure were obtained by reading from the curves drawn from the results

of the observations, the readings being then multiplied by different factors to bring them to amperes, according to the shunt used on the galvanometer.

Saturation current from anode at 800° C. ($1 = 10^{-7}$ ampere)

Pressure mm.	O (Curve I)	CO after increasing to steady value	CO second series (Curve II)	O after decreasing to steady value	H	H after continued heating (Curve III)	H after longer heating	O after decreasing to steady value (Curve IV)	O after continued heating
8	1·33	9·23	7·60	0·73	103	4·22	3·01	0·46	0·22
6	1·61	9·98	8·90		103	3·70	2·75	0·49	0·23
4	1·94	11·6	9·98		101	3·06	2·24	0·55	0·25
3	2·06	12·7	10·6	0·99	97·1	2·64	1·97	0·57	0·26
2	2·13	12·7	10·9		74·0	2·19	1·63	0·52	0·24
1	1·70	10·9	10·1		46·5	1·64	1·37	0·33	0·19
·5	1·35	9·52	8·63		24·6	1·38	1·12	0·24	0·16
·15	·71	6·26	5·96		8·2	1·16	·95	0·15	0·11
·05	·38		4·17		4·9	·99	·73	0·13	0·09

The final values of the positive leak in oxygen and in hydrogen, given in the table, seem to indicate that the leak had been gradually decreasing with time all through the series of observations, which occupied about six weeks. I believe that this decrease is largely due to the phosphate being gradually removed from the surface of the platinum strip, partly perhaps by sputtering, and partly by the continual bending backwards and forwards which the strip undergoes when it is alternately heated and cooled. That the phosphate was gradually disappearing appears to be indicated by the altered form of the current-pressure curve in oxygen. Although a pressure of maximum leak is still noticeable at between 2 and 3 mm. in Curve IV, it is much less marked than in Curve I. Neither H. A. Wilson nor Richardson obtained this maximum in their experiments with platinum, so that it would seem to be an effect of the phosphate used in the present experiments. This is also borne out by the fact that Garrett obtained similar results with aluminium phosphate.

It will be observed from the table that heating in carbon monoxide, and also in hydrogen, had the effect of greatly reducing the positive leak in oxygen. That hydrogen had a large effect in increasing the positive leak from platinum and from palladium was observed by H. A. Wilson*, who also found that the leak fell away very rapidly with time. A similar effect was obtained by Richardson† for platinum, and he too found that heating in hydrogen produced a diminution in the steady positive leak in oxygen.

In Richardson's experiments with platinum he found that the positive leak in hydrogen gradually diminished until it was much smaller than that in oxygen. This was not the case in the present experiments, for it will be seen from the table that, even after the leak in hydrogen had been reduced to a very small value, it was much further reduced by pumping out the gas and admitting oxygen to the apparatus.

On changing the gas in the apparatus from carbon monoxide to oxygen, or from hydrogen to oxygen, the positive leak always began at more than the normal value for the latter gas, and gradually decreased as the more active gas diffused out of the anode. On the other hand, on substituting carbon monoxide for oxygen, the leak at first gradually increased with time as the carbon monoxide diffused into the heated phosphate. In the case of the change from oxygen to hydrogen, this rate of increase was probably so rapid that the condition of equilibrium was reached

* *Phil. Trans.*, A. vol. ccii. p. 243, 1903.
† *Phil. Trans.*, A. vol. ccvii. p. 44, 1906.

before the galvanometer could be adjusted for measuring the largely increased current.

These experiments show that the surrounding gas has a considerable effect on the positive leak from sodium phosphate, and the gradual increase or decrease in this leak which occurs on changing one gas for another, seems to indicate that it is not a case of the presence of the gas helping or hindering the escape of ions from the surface of the anode, but that the gas molecules themselves diffuse into the anode and take an active part in carrying the current from its surface.

On the Magnetic Susceptibilities of Certain Compounds. By A. E. Oxley, Trinity College. (Communicated by Prof. Sir J. J. Thomson, F.R.S.)

[*Received* 17 December 1910.]

1. The following investigation is confined to the compounds potassium ferrocyanide, potassium ferricyanide, and the carbonyls of iron and nickel. Some years ago Prof. J. S. Townsend* showed that the magnetic susceptibilities of the ordinary ferrous and ferric salts in solution were accurately proportional to the amount of iron contained in one c.c. of the solution, and that for all these salts the ratio of the susceptibility of ferric iron to that of ferrous iron was constant. But solutions of the double salts potassium ferrocyanide and potassium ferricyanide in water had diamagnetic susceptibilities which, according to Townsend, were indistinguishable from the value for pure water. It was considered necessary to reinvestigate the two double cyanides, using a more delicate means of determination, and it was hoped that a determination of the susceptibilities of the carbonyls† would throw some light on the character of the metallic atoms which enter into their constitution. Since only small quantities of the carbonyls were available and also on account of their peculiar properties, the method briefly described in the following pages was adopted. This method is a modification of the one used by the late Prof. Curie‡, which consists in measuring by torsion the extent of the displacement which the substance under investigation experiences when placed in a strong magnetic field.

2. *General outline of method and apparatus.* A small quantity of the substance to be examined was placed in a glass phial, which was suspended from one point of a torsion arm. The phial and its contents were subjected to the field of a du Bois electromagnet, and the consequent displacement of the phial measured by a double suspension mirror attached to the end of the torsion arm remote from the phial. To prevent disturbances due to air currents it was necessary to surround the torsion arm and double suspension mirror as completely as possible by a metal box. This box was rigidly fastened to a brass carrier (provided with a screw motion) which slid upon rails. Thus it was easy to take the phial out of the field and also to adjust its position when in the field. For each determination the phial was brought to the

* J. S. Townsend, *Phil. Trans.*, A. 1896, p. 533.

† These have already been shown to behave diamagnetically by Sir J. Dewar and H. O. Jones, *Proc. Roy. Soc.*

‡ Curie, *Annales de Chim. et de Phys.*, Sér. VII. 5, 1895.

same position in the field, and by a preliminary series of observations this position was the one for which the effect on the phial was a maximum. Observations consisted in taking readings of the deflections produced when a known magnetic field was applied, then by a comparison of these deflections for different substances for the same field intensity, the susceptibility could be found, assuming a knowledge of the susceptibilities of air and water.

3. *Details of the apparatus.*

(α) *The electromagnet.* A sufficiently strong field could be obtained using flat pole pieces. The amount of residual magnetism was determined by means of a Grassot fluxmeter and was found to be negligibly small.

(β) *The torsion arm.* This was supported by a quartz fibre attached at the point *A*. It was necessary to preserve equilibrium of the torsion arm, since the masses under investigation were different, and this was done by means of a rider which could be slid along the portion *BC* of the arm.

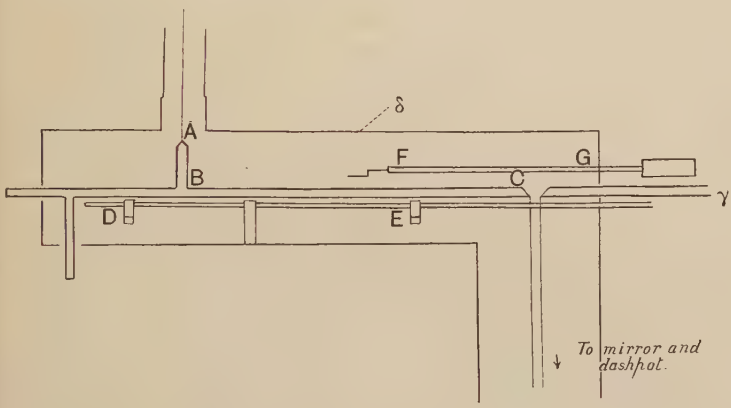


Fig. 1.

(γ) *Stage* provided with a three-dimensional adjustment for adjusting the double suspension mirror.

(δ) The metal box enclosing the torsion arm was provided with two windows, one for observing the position of the rider, and the other for viewing the mirror. The latter window was made of a thin sheet of mica. A means of resting the torsion arm so as to preserve the quartz fibre when the phial was being replaced was provided by the rod *DE* carrying two cranks, which came up from below as the rod was rotated and *slightly* raised the arm. The rider could be moved from outside by aid of the rod *FG*, just as for a balance with rider.

(ϵ) *The phials.* These consisted of glass bulbs, varying in capacity from 1 to 1·3 c.c., and were of two kinds, (*a*) for liquids, (*b*) for solids.

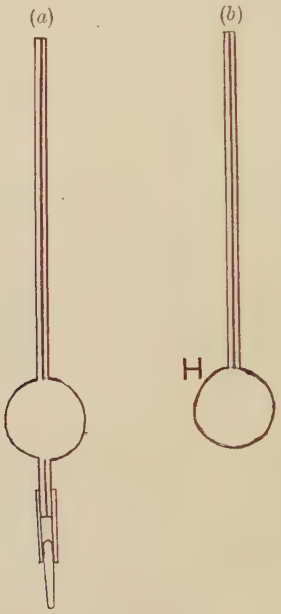


Fig. 2.

The phials (*a*) were provided with inlet and outlet tubes of fine bore, the outer diameter of the tubes being about 2 mm. The small internal diameter of the inlet and outlet tubes allowed only the minimum contact of the substance under investigation with the air—a precaution necessary in working with nickel carbonyl. The stoppers consisted of short pieces of indiarubber tubing closed by glass plugs. By this device the bulbs could be thoroughly cleaned and easily filled. To fill the phial the stopper was removed and the liquid drawn into the bulb. By tilting the bulb slightly the liquid ran out of the shorter limb and the stopper was placed in position. The liquid in the longer limb was removed by means of a fine capillary tube. In this way it was possible to obtain a sphere of the liquid under investigation.

(*b*) The phials for use with solids.
The solid was introduced through the hole H.

4. If a body of mass M, specific susceptibility χ, be placed in a field of intensity H the potential energy is

$$W = -\tfrac{1}{2} M\chi H^2.$$

Hence the force in any direction r is

$$F = -\frac{\partial W}{\partial r} = M\chi H \frac{\partial H}{\partial r}.$$

If the centre of the phial be on the same level as the centres of the pole pieces, and if Y, X be the forces along and perpendicular to the axis, then

$$X = M\chi \left(H_x \frac{\partial H_x}{\partial x} + H_y \frac{\partial H_y}{\partial x} \right),$$

$$Y = M\chi \left(H_x \frac{\partial H_x}{\partial y} + H_y \frac{\partial H_y}{\partial y} \right),$$

H_x, H_y being the components of field intensity along the directions of X and Y respectively. For the symmetrical position of Curie, H_x is small, also $\frac{\partial H_x}{\partial x}$ is small.

Hence $$X = M\chi H_y \frac{\partial H_y}{\partial x}.$$

No displacement was produced in the direction of Y because the resistance to motion is great. The position of the phial for which the force X was a maximum was found to be nearly constant for the range of field used in the experiments. In the following table a is the current in amperes, b the position of phial (on a fixed scale) when the deflection was a maximum, D is the deflection of the phial in scale divisions, and t is the temperature.

a	b	D	t
7·25	288·6	163·5	17·8
7·99	287·1	184·3	17·8
8·57	288·6	199·5	17·8
9·23	287·1	214·4	17·8
10·00	288·6	228·0	17·8

The mean position 287·8 was the one to which all phials were brought, the effect being a maximum then, and error due to displacement a minimum.

Let d_1 be the deflection due to phial alone.
„ d_2 „ „ „ phial and water.
„ d_3 „ „ „ phial and liquid.
Let χ_a be the specific susceptibility of air.
„ χ_ω „ „ „ water.
„ χ „ „ „ liquid.

Now $$X = M\chi H_y \frac{\partial H_y}{\partial x}.$$

Also $X = pd$, where d is the deflection and p* is some constant. Hence we have

$$p(d_2 - d_1) = (\chi_\omega m_\omega - \chi_a m_a) H_y \frac{\partial H_y}{\partial x} \quad \ldots\ldots\ldots(\alpha),$$

$$p(d_3 - d_1) = (\chi M - \chi_a M_a) H_y \frac{\partial H_y}{\partial x} \quad \ldots\ldots\ldots\ldots(\beta),$$

where M is the mass of the liquid taken, M_a the mass of air which fills the same volume; m_a is the mass of the air which fills the volume m_ω occupied by the water.

Now if for each of the observations the current be kept constant, then since there is no appreciable residual magnetism the field will keep constant, i.e. $H_y \frac{\partial H_y}{\partial x}$ will be constant. Hence, dividing (β) by (α),

$$\chi M = \chi_a M_a + (\chi_\omega m_\omega - \chi_a m_a) \frac{d_3 - d_1}{d_2 - d_1} \quad \ldots\ldots\ldots(\gamma).$$

Water, which had been distilled four times, was used as the calibration liquid, and a sufficiently large deflection could be obtained with one c.c. In the reductions, the susceptibility of air per unit volume was taken to be $+ 0{\cdot}25 \times 10^{-7}$ and the specific susceptibility of water as $- 7{\cdot}5 \times 10^{-7}$.

Preliminary experiments. Several preliminary experiments were made on Toluene, Benzene, Amyl alcohol, and Cymene. Below the results are compared with the values of the specific susceptibility given by Pascal†.

Liquid	$-10^7\chi$	$-10^7\chi$ (Pascal)
Toluene	7·60	7·65
Benzene	7·38	7·41
Amyl alcohol	8·36	8·43
Cymene	8·15	8·08

The iron carbonyl, $Fe(CO)_5$. The weight of iron carbonyl taken was 0·6207 gram. The weighing and determination were carried out as rapidly as possible and in a feeble light to avoid decomposition. The observations were made at a temperature of

* This is only true if the deflection of the torsion arm is small, which was always the case.

† Pascal, *Annales de Chim. et de Phys.*, Sér. VIII. 19, 1910.

19° C., for which temperature the density of iron carbonyl is 1·462. Using the relation (γ), the value of the specific susceptibility of iron carbonyl is found to be

$$\chi = -4{\cdot}00 \times 10^{-7}$$

at 19° C.

The nickel carbonyl, $Ni(CO)_4$. The carbonyl was first distilled at about 40° C. to remove traces of water, the distillation being carried out in an atmosphere of carbon dioxide. After distillation the receiver was corked up and the determination of the susceptibility proceeded with immediately. The weight of nickel carbonyl taken was 0·8914 gram*. Taking the density as 1·356 at 19° C., we find from (γ) that

$$\chi = -4{\cdot}81 \times 10^{-7}$$

at 19° C.

The double cyanides of iron and potassium. One or two large crystals of the salt were placed in a phial of the type (*b*) and the determination proceeded with as in the case for liquids. The specific susceptibility of *potassium ferrocyanide* was found to be

$$\chi = -4{\cdot}23 \times 10^{-7}.$$

The weight of crystals was 1·0621 grams, and their density was taken as 1·830.

For *potassium ferricyanide* the specific susceptibility was found to be

$$\chi = +93{\cdot}83 \times 10^{-7}.$$

Weight of crystal was 0·2165 gram and density was taken as 1·822.

It is clear from these results that iron in the acid radical behaves very differently from basic iron, but still there is some fundamental difference between these two similarly constituted salts which is marked by their widely different magnetic properties. It should be remembered that the specific susceptibility of potassium is $+44{\cdot}2 \times 10^{-7}$, and therefore the presence of the potassium groups in the compounds is of primary importance, and possibly of more importance than the iron atoms, so far as the magnitude of the paramagnetic susceptibility is concerned. Now potassium ferricyanide crystallises in the anhydrous state while potassium ferrocyanide crystallises with three molecules of water. Further, by considering the conductivity of a solution of potassium ferrocyanide in water Jones and Bassett† have shown that the

* This was the mean of the weights before and after the determination which were slightly different, probably due to evaporation.

† Jones and Bassett, *American Chemical Journal*, vol. xxxiv. 1905.

dissociation of potassium ferrocyanide takes place according to the reaction

$$K_4 Fe(CN)_6 \rightleftarrows \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{-}{CN}, \overset{-}{CN}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{Fe(CN)_3},$$

and comparing the conductivity of a solution of potassium ferricyanide with the values obtained for the ferrocyanide they concluded that potassium ferricyanide dissociates thus:

$$K_3 Fe(CN)_6 \rightleftarrows \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{Fe(CN)_4}.$$

The following explanation of the values found for the susceptibility is tentative. If we attach a divalent element or group of elements to an iron atom to form a ferrous salt, then the susceptibility immediately falls to a much smaller order of magnitude. We may perhaps picture this as due to the withdrawal of one or more corpuscles from the iron atom by the chemical union. In an atom possessing a resultant magnetic moment we probably have two systems of corpuscles revolving in opposite directions, and the resultant moment is due to the excess of the moment due to one system over that due to the other. If the corpuscle which is held up by the chemical union belonged to the system possessing the greater number of corpuscles, then chemical combination would reduce the resultant magnetic moment, which is essential for paramagnetism; and consequently the paramagnetic susceptibility would fall. Thus in the case of potassium ferricyanide in the solid state, part of the paramagnetic susceptibility would be due to the potassium and part due to the group $Fe(CN)_4$. We know that if a salt be dissolved in water the ions produced become associated with water molecules and each ion becomes loaded up so to speak to an unknown extent. Hence when potassium ferricyanide is dissolved in water the $\overset{+}{K}$ ions become associated with an unknown number of water molecules and so do both of the other ions $\overset{-}{CN}$, and $\overset{-}{Fe(CN)_4}$. Since paramagnetism depends upon the facility of orientation of the molecular axes, this association effect will tend to reduce paramagnetism; for the resultant magnetic moment is not increased (and is probably much reduced) by the association, therefore the controlling force is not increased while the system to be orientated has a greater inertia.

If we regard the effect produced by water of crystallisation as similar to that produced by the solvent water described above, then we not only see why there is very little change produced in the specific susceptibility of potassium ferrocyanide *crystals* when they are dissolved in water, but we also see why two similarly

constituted solid salts as the two double cyanides of iron and potassium possess so widely different magnetic susceptibilities. The difference is attributed to the molecules of water of crystallisation on this view.

In a similar manner the apparent high valency of iron and nickel in the carbonyls $Fe(CO)_5$ and $Ni(CO)_4$ would be indicative of a low susceptibility and high degree of chemical instability.

It is just conceivable, however, that since paramagnetism and diamagnetism are of a totally different nature, the small susceptibilities found by experiment might be due to two larger susceptibilities of a para- and diamagnetic nature superposed. This could be tested by aid of Langevin's* theory, according to which paramagnetism varies with the temperature while diamagnetism does not. The experiments described above were therefore repeated and the susceptibilities determined for several temperatures over a range of temperature of about 80° C. On account of the low boiling point of nickel carbonyl (43° C.) it was decided to work at temperatures below that of the atmosphere, and the range of temperature was from $+15°$ C. to $-60°$ C. The phial was surrounded by a thin-walled glass tube sealed at the lower end, and outside this was a Dewar flask containing petroleum ether. By pouring liquid air into the petroleum ether a temperature of about $-80°$ C. was produced and the flask was now placed in position surrounding the phial†. The temperature was measured by a small platinum resistance thermometer whose bulb was just clear of the phial. The thermometer was provided with compensating leads, and temperatures were read on a bridge wire in the usual way. The rate of rise of temperature was small and about ten determinations corresponding to ten different temperatures were obtained. Finally a similar set of readings was taken for the phial alone. In the case of potassium ferricyanide the curve representing the variation of susceptibility with temperature was approximately hyperbolic. The susceptibility of the glass of which the phial was made also increased with fall of temperature. The curves for the three compounds potassium ferrocyanide, iron carbonyl, and nickel carbonyl were practically parallel to the axis of t, showing that the susceptibility found above is not due to the superposition of a larger diamagnetic coefficient upon a nearly equal paramagnetic coefficient.

The curves in Fig. 3 show the variation of susceptibility with temperature.

* Langevin's theory really applies to gases only. The extension to liquids and solids which are paramagnetic has been given by Weiss.

† For this method of producing low temperatures I am indebted to Mr Hughes.

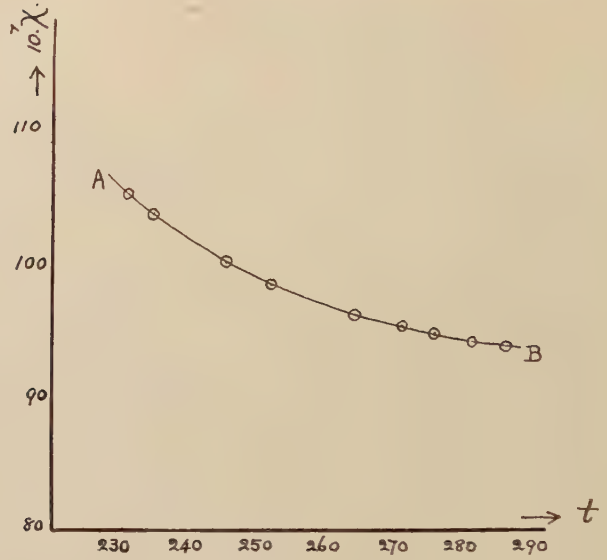


Fig. 3 (*a*).

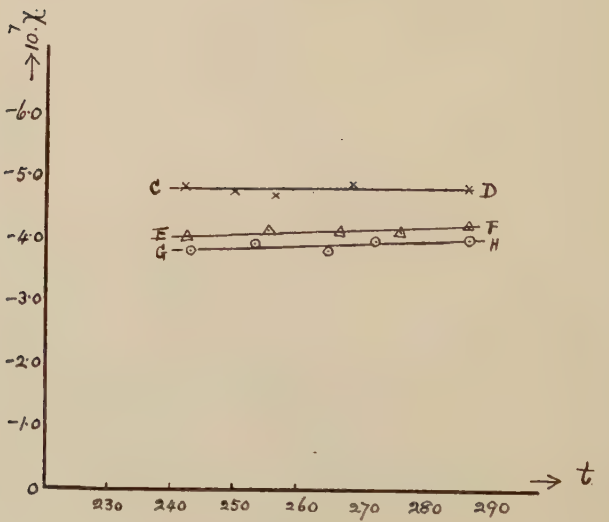
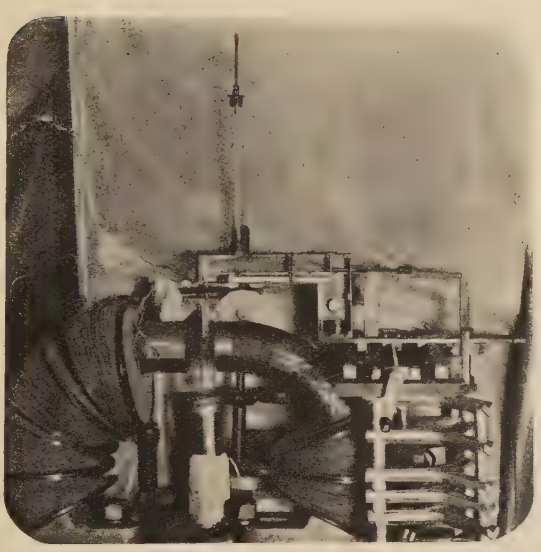


Fig. 3 (*b*).

Fig. 3 (*a*). Curve *AB* is for potassium ferricyanide.
Fig. 3 (*b*). Curve *CD* is for nickel carbonyl.
,, ,, *EF* ,, potassium ferrocyanide.
,, ,, *GH* ,, iron carbonyl.



In conclusion, I wish to give my best thanks to Prof. Sir J. J. Thomson for the great interest he has taken in this work; also I must express my indebtedness to Mr H. O. Jones, who has kindly supplied me with samples of the iron and nickel carbonyls.

On the distribution of the Secondary Röntgen Radiations round the radiator. By J. A. CROWTHER, M.A., St John's College.

[*Read* 28 November 1910.]

In the course of an investigation into the energy of secondary radiation from a substance under the influence of Röntgen rays, it was found necessary to determine the relative intensity of the secondary rays in different directions round the radiator. The present paper gives a preliminary account of the experiments made and the results obtained.

The radiations from a substance under the influence of Röntgen rays may be divided in general into two classes, (i) the "scattered" radiation, and (ii) the "homogeneous" radiations, the former being distinguished by having the same absorbability as the radiation producing it; the latter by an absorbability which is independent of the primary rays and characteristic of the radiator. Both types of radiation have been investigated.

The apparatus devised for these experiments is indicated in Fig. 1. The ionization chamber P, cylindrical in shape, is closed at one end by a thin aluminium window ω, 4 cms. in diameter, to admit the radiations. As the amounts of secondary radiation to be measured were necessarily small, a fairly large chamber was used; and in order to obtain the "saturation" current with a reasonably low voltage, a system of plane electrodes e, e ... of thin aluminium leaf mounted on wire rings was employed, instead of the usual, but unsatisfactory, central wire electrode.

The chamber P was mounted on the circumference of a mahogany disc D, which could be rotated about a fixed axis A through its centre. A lead plate with a suitable circular aperture R, was mounted on the fixed axis A, and served to support the radiator. The radiator thus remained fixed, while the ionization chamber revolved round it with the window ω always facing the centre.

In order to make connection between the moving ionization chamber and the measuring electroscope (which it is most desirable to keep fixed if accurate measurements are to be made) the key K was mounted so that the brass rod b came directly over the axis of rotation of the disc. The distance between b and the electrode E was thus fixed, and the two could be connected in the usual way by a thin copper wire shielded from induction effects in an earthed tube.

The Röntgen ray tube was enclosed in a leaden box from which a narrow pencil, limited and defined by the lead stops

L, *L*, was allowed to emerge and impinge on the radiator *R*. The cross section of the beam at *R* was quite well defined when viewed with a fluorescent screen, and had a diameter of about

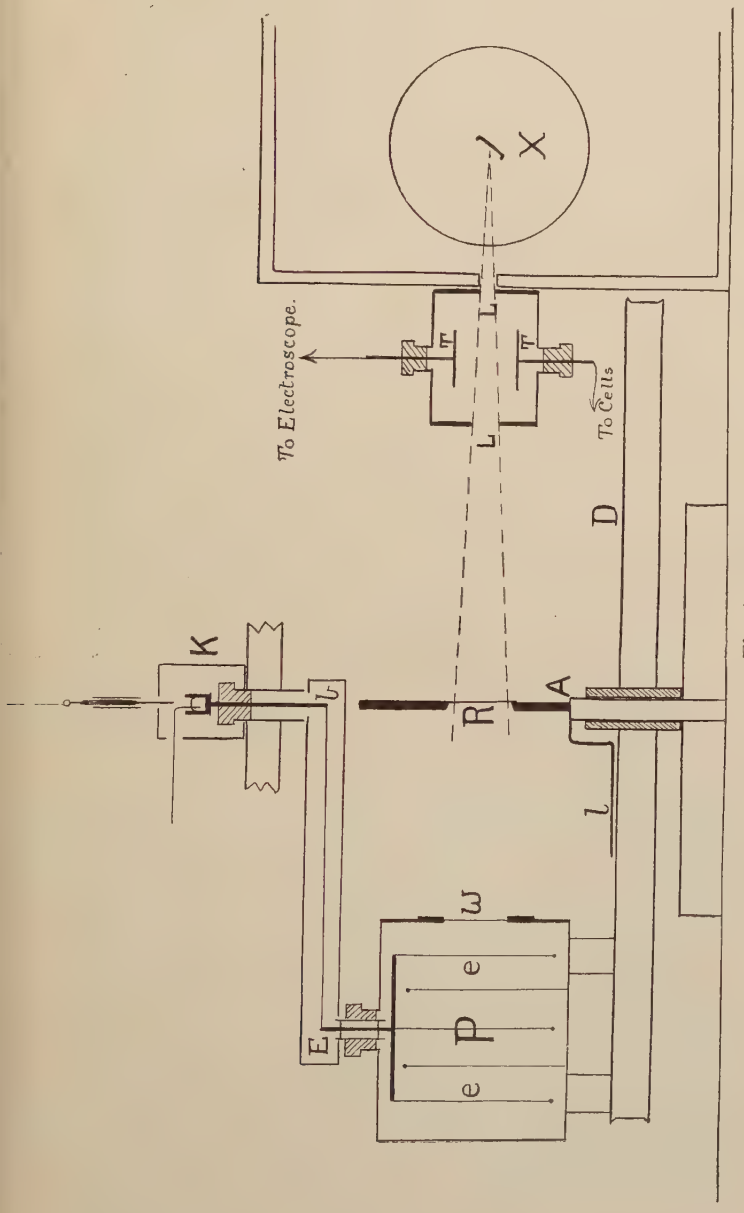


Fig. 1.

3 cms. The distance from R to ω was 15 cms., and the diameter of ω 4 cms.

Two parallel electrodes T, T were mounted in the tube LL. The ionization in the air between them was measured in the usual way by a second Wilson electroscope, and served to standardize the primary beam. The position of P with respect to the incident rays could be read off on a circular scale fixed to the disc D by means of a pointer l attached to the fixed axis A.

As it was necessary to know the distribution of the secondary rays in the direction of emergence of the primary beam, as well as of those which were returned from the radiator, the latter took the form of sheets of the given substance sufficiently thin to absorb only a small fraction of the incident radiation. The actual absorption could be allowed for, but it was desirable, owing to the difficulties of keeping an X-ray bulb absolutely constant, that the correction should be as small as possible.

The measurements were made as follows. The ionization chamber P was fixed in the required direction; the radiator was placed in position at the centre of the wheel, and the intensity of the ionization measured with the rays passing. The radiator was then removed, and the ionization while the primary rays were passing was again measured. A certain amount of secondary radiation is given out by the air through which the primary beam passes, some of which enters the ionization chamber P. There was thus always a small but perceptible current through P, even in the absence of the radiator at R. The difference of the readings with and without the radiator at R was taken as giving the true effect due to the radiator alone. The disc D was then rotated through a suitable angle and the readings repeated. In this way the intensity of the secondary rays all round the radiator could be mapped out.

The absorbability of the secondary rays could be determined by fixing P at some suitable angle and then interposing absorbing screens in front of the window ω. Similarly by placing P directly in the line of the primary beam and removing the radiator at R, the absorption of the primary rays could be measured.

The scattered radiation, which has the same penetrating power as the primary, has been regarded as being due to the forced vibrations of the electrons in the atom under the forces in the primary pulse. If i_θ is the intensity in a direction OP making an angle θ with the line of motion of the electron, then i_θ is proportional to $f^2 \sin^2\theta$, the component of the acceleration of the electron in the direction perpendicular to OP. If we assume that the accelerations of the electrons are distributed evenly in a plane perpendicular to the direction of the primary beam, it can be shewn that the intensity is a minimum in this plane, and rises

to a maximum both forward and backward in the line of the primary beam; the maximum value being twice the minimum.

The following figures (Table I) obtained with a radiator of filter paper (cellulose) will shew the distribution which actually obtains round a radiator emitting only scattered radiation.

TABLE I.

Scattered Radiation.

	θ	With Radiator	Without Radiator	Ion. due to Radiator	Correc. for absorption	I_θ
R.H. returned	35°	3·0	1·2	2·0	1·10	2·20
	50°	2·8	1·0	1·8	1·12	2·0
	70°	2·6	1·3	1·3	1·19	1·55
R.H. transmitted	25°	7·0	2·9	4·1	1·10	4·50
	40°	4·5	1·8	2·7	1·11	3·00
	60°	3·3	1·5	1·8	1·15	2·10
L.H. transmitted	30°	5·7	2·3	3·4	1·10	3·75
	50°	3·5	1·1	2·4	1·13	2·7
	70°	2·3	·9	1·4	1·20	1·7
L.H. returned	35°	3·0	1·0	2·0	1·10	2·20
	55°	2·7	1 0	1·7	1·13	1·90
	70°	2·3	1·0	1·3	1·20	1·55

R.H. and L.H. signify the right-hand and left-hand positions of P, looking along the beam. "Returned" radiation is that which comes back from the radiator on the side nearest the focus tube; "transmitted" is that which goes forward and emerges on the far side of the radiator. θ is the angle made by the axis of P with the axis of the primary beam. The next two columns give the ionization in P with and without the radiator R. The difference of the two gives the effect due to the radiator itself. The next column gives the correction factor for the absorption of primary and scattered rays in the radiator. This may be calculated as follows. Consider any element of unit area at a depth y in the radiator. Then if λ is the coefficient of absorption for the rays, the intensity of primary radiation at y is $I_0 e^{-\lambda y}$, and if k is the fraction of the energy scattered per unit volume between the directions θ and $\theta + d\theta$ the intensity of the scattered radiation between these limits is

$kI_0 e^{-\lambda y} dy$. For the returned radiation the thickness of the material traversed by the scattered radiation is $y \sec \theta$; for the transmitted $(a - y) \sec \theta$, where a is the thickness of the radiator.

For the whole plate we have, therefore,

$$I_m = kI_0 \int_0^\omega e^{-\lambda y (1 - \sec \theta)} dy$$

for the returned radiation, and

$$I_m = k' I_0 \int_0^a e^{-\lambda y (1 - \sec \theta) - \lambda a \sec \theta} dy$$

for the transmitted radiation, where I_m is the measured intensity of the radiation.

The intensity I_θ if no absorption had taken place would have been simply $kI_0 a$. Evaluating the integrals we have

$$\frac{I_\theta}{I_m} = \frac{a\lambda (\sec \theta + 1)}{1 - e^{-a\lambda (\sec \theta + 1)}}$$

for the returned, and

$$\frac{I_\theta}{I_m} = \frac{a\lambda (\sec \theta - 1)}{e^{-\lambda a} - e^{-\lambda a \sec \theta}}$$

for the transmitted radiation.

The value of λ/ρ for filter paper for the rays used was 1·8. The values of these expressions for different values of θ are the correction factors given in the table.

The corrected values for I_θ are given in the last column of Table I, and are represented diagrammatically in Fig. 2. In this figure the radiator is at R, and direction of the incident primary beam is that of the arrow. Radii are drawn in all directions from R, the length of any radius being proportional to the intensity of the radiation I_θ along the direction of that radius.

We thus get a picture of the distribution of the scattered rays round the radiator in the plane of motion of the ionization chamber*.

It will be seen that the distribution so far agrees with that to be expected on the simple theory that the curve shews maxima in the backward and forward directions of the rays, and minima in a plane at right angles to that direction. It will be seen at once,

* In these experiments the focus tube was arranged so that the path of the cathode rays in it was perpendicular to the plane of rotation of the disc D. When the bulb was turned so that the cathode rays were in this plane there was always a preponderance of the scattered radiation on that side of the primary beam towards which the cathode rays were directed. This effect, which is due to a partial polarization of the primary Röntgen rays, has been observed before for the returned radiation. It does not affect the distribution of energy between the transmitted and returned radiation; and it was thought better to describe the more symmetrical case first.

however, that it is by no means symmetrical about this plane. At any inclination to the normal there is a preponderance of radiation in the forward direction, and this preponderance is greater the more nearly we approach the direction of the primary rays. Experiments made with aluminium radiators gave similar results.

The shape of the curves suggested that the effect might be due to two types of radiation, one scattered according to the simple theory, and the other going mainly in a forward direction.

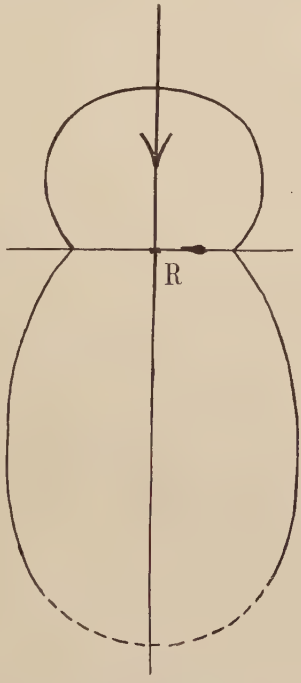


Fig. 2. Distribution of Scattered Röntgen Radiation.

It will be seen from the figure that for the returned radiation the maximum in the direction of the primary beam (obtained by interpolation between the 1st and 4th quadrants) is almost exactly twice the minimum value in the direction perpendicular to it.

Various attempts have been made to separate the radiation into two parts, but without any success. The experiments so far made are briefly as follows:

(i) The window of the ionization chamber P was covered with sufficient aluminium board to cut down the radiation entering the chamber by more than one half. The relative ionizations in the forward and backward positions of P were found

to be practically unaltered by this arrangement. The actual values obtained for the coefficients of absorption of the transmitted and returned radiations in aluminium were 11·3 and 10·7 respectively. The difference between these values is not greater than the experimental error.

(ii) Experiments were made to discover if the thickness of the radiator had any effect upon the distribution of the scattered radiation. Radiators of four, seven, and twelve sheets of filter paper were employed. The distribution was found to be the same for the three radiators.

(iii) Experiments were also made with aluminium radiators. The distribution of the scattered radiation was very similar to that for paper, but the preponderance in the forward direction was even greater. Measurements were also made of the scattered radiation from copper; the soft homogeneous radiation being totally absorbed in aluminium before reaching the chamber *P*. Owing to the great absorbability of the primary rays in copper, very thin sheets had to be used and the residual radiation after absorbing the characteristic rays was very small. However, even here the readings shewed a marked preponderance of the scattered radiation in the forward direction. Experiments with tinfoil in which the primary rays were made sufficiently soft to excite no appreciable characteristic radiation also shewed a similar distribution of the scattered rays.

These results are briefly summarized in the following table which gives the intensity of the transmitted and returned scattered radiations, for an angle θ of 30° with the primary rays, for different radiators.

TABLE II.

Radiator	Transmitted	Returned	$\frac{\text{Transmitted}}{\text{Returned}}$
Filter paper:			
4 sheets	2·1	1·0	2·10
7 sheets	4·5	2·2	2·05
7 sheets (scattered radiation cut down by aluminium)	2·0	1·0	2·00
12 sheets	6·4	3·1	2·05
Aluminium	10·5	3·3	3·2
Copper (scattered) ...	1·28	·63	2·0
Tinfoil (scattered) ...	11·4	5·3	2·2

The distribution of the homogeneous characteristic secondary radiation has also been measured using a copper radiator. The following table (Table III) gives the results obtained. Readings

TABLE III.

Distribution of "characteristic" radiation from a Copper Radiator.

	θ	With Radiator	Without Radiator	Ion. due to Radiator	Ion. due to scattered rays	Ion. due to characteristic radiation	Correction factor for absorption	I_θ
R.H. Returned	35°	15·2	1·0	14·2	·3	13·9	1·26	17·5
	50°	14·7	·7	14·0	·3	13·7	1·33	18·2
	70°	12·0	·8	11·2	·2	11·0	1·56	17·2
R.H. Transmitted	25°	17·0	2·1	14·9	·6	14·3	1·24	17·6
	40°	15·3	1·1	14·2	·4	13·8	1·32	18·2
	50°	14·6	·9	13·7	·3	13·4	1·35	18·1
	60°	13·4	·9	12·5	·3	12·2	1·40	17·1
L.H. Transmitted	30°	15·2	1·0	14·2	·5	13·8	1·26	17·4
	50°	13·7	·6	13·1	·3	12·9	1·35	17·4
	65°	11·8	·5	11·3	·3	11·5	1·55	17·8
L.H. Returned	35°	15·0	·8	14·2	·3	13·9	1·26	17·5
	65°	12·8	·7	12·1	·2	11·9	1·50	17·8

are made as before for different inclinations θ, with the primary beam, with and without the copper radiator. Correction is then made for the ionization due to the scattered radiation from the copper, which can be measured separately by interposing sufficient aluminium board in front of the window ω to absorb all the soft

characteristic rays. The correction for the absorption of the primary and secondary rays in the copper sheet for the different angles is calculated (allowance being made for the fact that the coefficient of absorption is now no longer the same for the two streams of radiation). The last column gives the corrected intensity of secondary characteristic radiation, in the direction θ, for a copper radiator of thickness ·00075 cm.

It will be seen at once that the distribution of the characteristic radiation is practically uniform all round the radiator. The values of I_θ given in the last column do not differ by more than the possible errors of experiment. The characteristic radiation, therefore, is emitted equally in all directions.

Summary.

The distribution of the secondary Röntgen radiations has been measured for both scattered and characteristic radiations. The scattered radiation reaches a maximum both forward and backward in the direction of the primary beam, and falls to a minimum at right angles to that direction. At any given inclination to the primary beam there is always a preponderance of radiation in the forward direction, that is to say on the opposite side of the radiator to that upon which the primary rays first fall. This preponderance increases the nearer we approach the direction of the primary beam.

The characteristic secondary radiations are emitted equally in all directions round the primary beam.

A New Method of Investigating the Positive Rays. By Prof. Sir J. J. Thomson.

[*Read* 31 October 1910.]

In this method the rays are received on a photographic plate inserted inside the discharge tube and placed in a light-tight case until it is wished to photograph the rays, when the plate is lifted from its case by a mechanism worked from the outside and the rays are allowed to fall upon it. It is found that a photographic plate is very sensitive to the rays; a pencil of these only one-third of a millimetre in diameter gave a good photograph in less than five minutes. The photographic plate besides being much more sensitive than the willemite screen hitherto used by the author has the advantage of giving a permanent record and allows of greater accuracy of measurement. Using this method the author has detected in the positive rays in addition to the atom and molecules described in his paper in the October number of the *Philosophical Magazine*, positive rays of a secondary nature having values of m/e, 1·5, 2·5, etc. that for the hydrogen atom. Photographs taken by this method were exhibited at the meeting.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

Note on Strongylocentrotus lividus as a Rock-borer. By JAMES ROMANES, B.A., Christ's College.

[*Received* 20 January 1911—*Read* 6 February 1911.]

(PLATE II.)

Reference has been made from time to time to the fact that the echinoid *Strongylocentrotus lividus* is capable under certain circumstances of boring into rocks in much the same way as the Molluscs *Pholas* and *Lithodomus* do. It is fully discussed in a communication by M. Ch. Lory* who records instances from the coast of Brittany, but these all occur in very friable or weathered rock "in the state which precedes its reduction to sand." He sums up his observations by saying, "Thus whatever be the nature of the rock, the property of becoming friable, at any rate by continuous submergence, is the condition necessary to enable the echinoids to excavate it." In the discussion on the above paper there is a long communication by M. Cailliaud in which he denies that the echinoids play any part in the formation of the holes in which they live.

It is well known that the same species of echinoid occurs on the west coast of Ireland, but that some doubt exists as to their capabilities as rock-borers is shown by the following quotation from the volume of the *Cambridge Natural History* (Vol. II.) on Protozoa, Coelentera and Echinoderma, page 541. "*S. lividus*

* *Bull. Soc. Geol. France*, Ser. 2, Vol. XIII. 1855, p. 44.

occurs abundantly in the Mediterranean and reaches the English Channel and the west coast of Ireland. In the last named locality where it is exposed to the full swell of the Atlantic it is said to excavate holes for itself in the limestone rocks, about 10 inches in depth." To this there is appended a footnote as follows:— "Mr E. W. L. Holt, scientific adviser to the Irish Board of Fisheries, casts doubt on much of this supposed excavation; while disclaiming any novelty in this observation, he points out that in many cases one side of the cavity is formed by calcareous algae and it seems as if the animal wanders into a crevice in which it is imprisoned by the growth of this plant." While working on the geology round the coast of Glengarriff, Bantry Bay, I noticed that many of the shallow pools left between tide marks were inhabited by hundreds of these echinoids, which in certain cases appeared to have sunk themselves more or less deeply into the rocks at the bottom of the pools. In most cases the echinoids are arranged in fairly well defined lines parallel to the strike of the rocks which are here practically vertical: this no doubt is due to slight differences in the character of the rock.

I was fortunate enough to find a case where the echinoids were adhering to the vertical sides of the pool and by driving a wedge in along the line of cleavage was able to obtain a slab of rock with several specimens on it.

The specimen figured is part of this slab and measures roughly 20 cm. × 15 cm. × 6 cm., on it are three individuals in clearly defined excavations while there are portions of two other excavations which were inhabited when the specimen was collected.

The rock is an *unweathered*, fine-grained, compact, slaty mudstone, cleavage being rather imperfectly developed. When treated with dilute hydrochloric acid the rock shows no effervescence so that the amount of calcareous matter present must be very small, certainly not enough to cause disintegration of the rock, on removal by acid.

In the specimen there can be absolutely no doubt that the borings are in the rock, the bare surface being exposed on all sides. The two largest excavations are 5·5 cm. in diameter and about 3 cm. in depth, having the form of an almost perfect hemisphere with a remarkably smooth surface.

The third occupied excavation though the smallest in diameter (4 cm.) is considerably deeper in proportion than the others and in this case the echinoid is completely below the general level of the rock, and there seems to have been an effort on the part of the echinoid to regain a horizontal position since the excavation is considerably deeper on one side than the other. One of the unoccupied hollows from which an echinoid was removed shows numerous *Serpulae* and *Fenestella*-like polyzoa adhering to the

rock. This certainly suggests that the echinoids after boring to a certain depth definitely stop sinking themselves any further, otherwise any continued chemical or mechanical action would inevitably destroy these organisms which seem to be living in security below the echinoid.

The specimen also shows the calcareous algous growth which in some cases, as pointed out by Mr Holt, grows up round the echinoid and may imprison it, giving a false impression of boring. At times this calcareous covering extends some distance over the surface of the excavation, so that at first sight it appears as if the rock were covered by a thick layer of algous growth, but in reality this covering is, in the excavations themselves, rarely more than 1 mm. in thickness. It is noticeable however that the limpet on the specimen is in a distinct depression, and that in this case the appearance is caused by the algous growth rising up around it, not by any active boring on its part.

A few other observations made from an examination of numerous other pools inhabited by *S. lividus* are perhaps worth recording.

There seems to be no connexion between the diameter and the depth of the excavation, while in every case the size of the excavation is exactly fitted to the size of the individual. Whether the action is a fairly rapid one, each individual excavating a hollow to the desired depth, or whether the action is the result of generation after generation of echinoids each slightly deepening the excavation made by a predecessor, is impossible to say. Where the pools are in a hard massive grit which is the dominant rock type along that part of the coast there is never the least tendency for hollows to be formed, though it may be noticed that the echinoids tend to seek the shelter of any natural crevice or hollow in the rock. It is difficult in the absence of any observations over a prolonged period to say of what nature the excavating action is, but as the rock contains so little material soluble in weak acid it seems probable that the action is a mechanical rather than a chemical one, and is possibly due to constant movement of the spines, the ends of which can be seen in many cases to be considerably worn especially in the case of those specimens which inhabit hollows.

EXPLANATION OF PLATE II.

The Plate shows slab of slate with three echinoids in excavations. At the upper end is part of another hollow showing thin film of calcareous algae (unshaded portion). At the lower end of specimen is an excavation from which the echinoid has been removed to show the *Serpulae* growing below.

The effect of exposure to ultra-violet light on blood-serum. By W. M. Scott, Trinity Hall, John Lucas Walker Student in Pathology. (Communicated by Prof. G. Sims Woodhead.)

[*Read* 20 February 1911.]

During the past year, 1910, the chemical and biological effects of the ultra-violet rays of the spectrum have been the subject of considerable study, almost entirely in France. For example, Berthelot and Gaudechon* have described various simple organic syntheses and decompositions, Mlle Cernovodeanu and Henri† have shown their destructive effect on unicellular organisms and on tetanus toxin, tuberculin etc., while Baroni and Jonesco-Mihaiesti‡ have studied the effects on diphtheria toxin and on immune sera.

The results of the last observers indicated a possible important practical application in serum therapy. They found namely that horse serum treated by ultra-violet light could be robbed of its power of precipitating the appropriate anti-serum, and of producing in sensitive guinea-pigs the toxic manifestations which are grouped under the name of "anaphylaxis" or "serum-sickness." These toxic effects, though of relatively small practical importance when compared with the direct therapeutic benefit in diphtheria, are of much importance as the probable cause of the inefficiency of antibacterial sera as curative agents in infective conditions.

The question arises whether the antibodies in immune sera are capable of surviving a process such as the above which diminishes or removes their anaphylactic toxicity.

Baroni and Jonesco-Mihaiesti (*loc. cit.*) have stated that diphtheria antitoxin under the ultra-violet light rapidly loses its protective power. It seemed worth while for the reasons above-mentioned to repeat their experiments on these points. The source of ultra-violet light employed in my work was a mercury vapour electric arc at 100 volts, the tube consisting of quartz and transmitting a very high proportion of the ultra-violet part of the spectrum. The various sera treated were contained also in a quartz tube at a distance of 15 cm. from the source of light and kept cool by dipping in a water bath. The sera were in most

* *Compt. rend. Acad. Sciences*, 1910, T. CL. pp. 1169, 1327, 1517, 1690; T. CLI. pp. 395, 478.

† *Ibidem*, 1910, T. CL. pp. 52, 549, 729.

‡ *Compt. rend. Soc. Biol.* 1910, T. LXVIII. p. 393; T. LXIX. p. 273.

cases diluted 1 in 5 with normal saline (the action of the rays on undiluted serum was much less marked); the depth of fluid to be penetrated did not exceed 1 cm. and the tube was frequently agitated.

Serum exposed to the action of ultra-violet light under these conditions for about 5 hours loses its property of causing a precipitate with the corresponding anti-serum, the loss gradually progressing during that period till the serum, which before treatment produced a large precipitate even diluted 500 times, now fails to produce anything more than a doubtful turbidity in the dilution 1 in 5.

The effect on the immune body of the serum is equally marked. Rabbit serum containing a powerful haemolytic immune-body for ox blood (the minimum haemolytic dose for 1 c.c. of 1 p.c. ox corpuscles being 0·0005 c.c.) is completely robbed of haemolytic power after 4 hours' exposure, 0·1 c.c., *i.e.* 200 times the dose being now without any lytic effect.

The effect on antitoxin was estimated with a sample of high potency anti-diphtheria serum containing 1000 units per c.c. After 4 hours' exposure, though the precipitating property is still perceptible, the antitoxin falls to below $\frac{1}{5}$ of its original value, *i.e.* 5 times the minimum neutralising dose, determined on the control portion, just fails to protect a guinea-pig from the standard dose of toxin. A serum of high antitoxic potency has been converted into one of low potency.

The anaphylactic toxicity of the serum is apparently the property most resistant to the action of ultra-violet light. Even after 6 hours' exposure a small dose of the serum is capable of producing the typical death, a little delayed, in a highly sensitive guinea-pig. In guinea-pigs less sensitive, *e.g.* those passively sensitised with a small dose of precipitin serum, the reduction in toxicity is more apparent. The effect on intravenous injection is delayed and atypical. Instead of acute asphyxia with extreme emphysema of the lungs there is a peculiar progressive slowing of the respiration rate with large oscillations in the blood pressure before death, although the entrance and exit of air in the lungs remain free. The mechanism of this is a subject for separate investigation. Here it is sufficient to note that exposure to ultra-violet light sufficient to destroy the great proportion of the antitoxin leaves the serum in possession of an appreciable anaphylactic toxicity. It does not seem therefore that the method can be employed to get rid of the detrimental effects of therapeutic sera.

The passage of bacteria from the mouth to the lung. By L. Cobbett, M.D., Lecturer in Pathology, and G. S. Graham-Smith, M.D., Lecturer in Hygiene.

[*Read* 20 February 1911.]

Various observers have fed animals with tubercle bacilli, and have produced tuberculosis of the lungs, sometimes together with tuberculosis of the mesenteric glands and elsewhere, but at other times mainly affecting or even confined to those organs. Calmette and his pupils, and some who have followed him in this country, have concluded that in these experiments the tubercle bacilli which caused the pulmonary lesions had passed through the mucous membrane of the intestines into the lacteals, and so through the mesenteric glands into the thoracic duct, and hence into the systemic veins, right side of the heart, and pulmonary artery; and they have not hesitated to conclude from such experiments that the majority of cases of pulmonary tuberculosis in man are caused in this way.

We ourselves have for a long time doubted whether it is at all certain that in such experiments the bacilli reach the lungs by this route, and have suspected that micro-organisms placed in the mouth might sometimes find a shorter way to the lungs by the air passages, especially in experiments in which a stomach-tube was used for introducing the bacteria. In some experiments made by one of us, and already published*, *B. prodigiosus* was found in small numbers in the lungs of guinea-pigs fed with this micro-organism in 12 out of 16 animals, and yet in only one case was it found in the mesenteric glands. It therefore seemed unlikely that the bacilli found in the lungs could have passed through the mesenteric glands. In another series of experiments, guinea-pigs were fed with tubercle bacilli, killed a few hours later, and their various organs examined for tubercle bacilli by injecting emulsions into other guinea-pigs. In three of the six animals used, the bacilli were thus proved to have entered the lungs, and yet only in one of them were they present in the mesenteric glands. A guarded conclusion was drawn from these experiments; the author thought that in his experiments it was, on the whole, more probable that the bacilli had found their way through the trachea, rather than that they had been taken in through the intestine. We can now speak with more confidence, for in some recent experiments, which we now record, the bacilli were found in the lungs so soon after the animals were fed with them that it was impossible that they could have been absorbed from the intestine. The experiments so far concluded have been confined to very

* "Portals of Entry of the Tubercle Bacilli which cause Phthisis," L. Cobbett, *Journ. of Path. and Bact.* Vol. xiv. 1910, p. 563.

young guinea-pigs, but they show that a transference of bacteria placed in the mouth occurs in these animals quite normally, and surprisingly freely, and this makes it at least very probable that in older animals and in other species also, bacteria occasionally get into the lungs from the mouth in this way.

These experiments were as follows. Guinea-pigs, 16 in all, when for the most part only a day or two old, were fed with emulsions of *B. prodigiosus* in a small quantity of milk. The mixture was put into their mouths drop by drop, on a wire loop, much as one might feed an infant with a spoon. It was readily taken and swallowed quite naturally, without provoking any struggling or coughing, or indeed calling forth any resistance whatever. The quantity thus given was usually about 50 drops, and this represented the greater part of one or two young agar cultures. The feeding took about 10 to 17 minutes. At the end of this time the animals were killed and immediately cultures were made from their principal organs. The cultures were made by the method fully described in the paper previously referred to. Briefly the procedure was this: with due precautions portions of the various organs, weighing probably about half a gramme, were removed and crushed into a pulp between glass plates, and this pulp was then transferred to two agar tubes which were incubated at 22° C. In the case of the lung cultures nearly the whole of one organ, including some of the larger bronchi, was crushed to make the pulp for sowing the tubes. Cultures were made also from the contents of the stomach, and from the small intestine. As the latter was usually empty except for a small quantity of mucus it was sometimes washed out with salt solution.

In every experiment colonies of *B. prodigiosus* appeared in the lung cultures, usually in considerable numbers, clearly showing that the bacilli had reached the lungs, or at least the larger bronchi. A few colonies were obtained in some cases from the trachea also, though only very small quantities of mucus, wherewith to sow the culture tubes, could be obtained from this situation.

The stomach contents were pink with the bacilli, but in a few instances we failed to get a culture, usually because other more-rapidly-growing bacteria over-ran the surface of the culture medium.

In no case did colonies of *B. prodigiosus* appear in the cultures sown from the mesenteric glands.

In quite exceptional instances did one or two colonies of this microbe grow in tubes, sown from the liver, spleen or kidneys. It may be that the bacilli got into the organs through the lungs, though the time would appear too short; or it may be that they gained entrance into the tubes in consequence of some error of

Young guinea-pigs fed with B. prodigiosus.

Cultures from various organs. Only colonies of *B. prodigiosus* recorded.

No.	Age in days	Interval feeding and death	Lungs		Trachea	Liver	Spleen	Kidneys		Stomach	Small intestine	Caecum	Mesenteric glands	Method of killing
			R.	L.				R.	L.					
		minutes												
1	2	12	P	P	P	P	0	—	—	P	—	0	—	Chloroform
2	2	13	P	P	—	0	0	0	0	—	P	0	0	Ligation of neck
3	1	15	P	P	—	P	P (2)	0	0	P	P	0	0	,,
4	1	10	P	P	P	0	0	0	0	P	P	0	0	Chloroform
5	2	12	P	P	P	0	0	0	0	0	P	0	0	Ligation of neck
6	3	10	P	P	—	P	0	0	P (1)	—	P	0	0	,,
7	2	8	P	P	P (1)	0	0	0	0	P	0	0	0	,,
8	3	10	P	P	—	0	0	0	0	0*	0	0	0	Chloroform
9	1	12	P	P	P (few)	0	0	0	0	P	0	0	0	,,
10	2	10	P	P	P (7)	0	0	0	0	P	0	0	0	Ligation of neck
11	2	10	P (3)	P (6)	—	0	0	0	0	0	0	0	0	,,
12	2	11	P	P (5)	0	0	0	0	0	P	0	0	0	,,
13	2	15	P	P	0	0	0	0	0	P	0	0	0	,,
14	4	17	P	P	0	0	0	0	0	0†	0	0	0	Clamp
15	5	15	P	P	—	0	0	0	0	0†	0	0	0	,,
16	2	8	P	P	—	0	0	0	0	P	P	0	0	,,

* Contents of stomach pink with *B. prodigiosus.* † Overgrown with film-forming bacteria.

P = Many colonies of *B. prodigiosus* appeared on the culture tubes sown from the organ. When only one, or a very few colonies of *B. prodigiosus* appeared, the number of these colonies is indicated by a figure in brackets.

0 = No colony of *B. prodigiosus.* Other colonies which occasionally appeared on the tubes are omitted.

technique. On this point one must reserve one's judgement until further evidence is available.

The important result of the experiments is that the bacteria placed in the mouth gained entrance into the lungs of these very young animals, constantly, and in considerable numbers, and that too within a space of time, measured by 10—17 minutes from the commencement of feeding to the last respiratory movement, which is clearly too short to allow of their having been carried round by the intestines and their lymphatics. The bacilli must therefore have travelled to the lungs through the trachea and bronchi. In support of this we may add the recovery of the bacilli from the trachea in some cases, as already mentioned.

In the earlier experiments of this series the animals were killed by chloroform, and it was noticed, that just as they were dying they would give several deep gasping inspirations. It was suggested that the abnormal inspirations might be the cause of the bacilli passing from the mouth and pharynx into the lungs in a way which might never have occurred if the animals had been allowed to live. In order to meet this objection it was necessary to kill the animals in a special way. The method next used was to tie a ligature tightly round the neck of the animal so as to occlude the trachea. It was found that this procedure usually resulted, in the case of these newly born animals, in dividing the spinal column, and with it the cord, without cutting through the skin. This was not altogether a disadvantage, because the division of the spinal cord completely inhibited all subsequent respiratory movements. In later experiments the animals were killed by the sudden application of a blunt-jawed clamp to the neck which acted very much like the ligature.

The experiments confined so far to guinea-pigs will be extended to other animals. We are of opinion that what they have clearly established in young guinea-pigs, namely, the constant passage of bacteria placed in the mouth directly, by way of the air passages, into the lungs, makes it exceedingly probable that a similar passage of bacteria into the lungs by this route takes place in older animals also, and in other species. We believe that this is the true explanation of many of those experiments in which tuberculosis has originated in the lungs of animals fed with tubercle bacilli, and that our experiments invalidate the conclusions drawn from such experiments as to the absorption of bacteria from the intestine in general, and the usual path of infection in pulmonary tuberculosis in particular.

It may perhaps be well to add that we do not for a moment wish to deny that tuberculosis may arise in consequence of bacilli being absorbed from the intestine. We have seen many such cases, especially in children.

On Regularities in the Spectrum of Neon. By HERBERT EDMESTON WATSON, B.Sc. (London), Trinity College, Cambridge, 1851 Exhibition Scholar, University College, London. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 13 March 1911.]

In 1908 the author published a paper on the "Spectrum of the Lighter Constituents of the Air*" in which were given the wave lengths of a number of lines ascribed to neon. As the primary object of the research was to detect, if possible, the presence of a new gas, long exposures were given to the plates, and the accuracy of the measurements was consequently somewhat impaired. It was considered, however, that the values given for the wave lengths were usually correct to 0·03 A.U., and this was borne out by the agreement with the previous measurements by Baly†.

The existence of some 200 new lines was determined by these experiments, making the total 321, and it seemed worth while to examine the spectrum with a view to discovering a possible regularity. For this purpose, the wave lengths were first converted into the corresponding oscillation frequencies *in vacuo*.

Since the helium spectrum had been found to be capable of resolution into six series of lines with gradually diminishing intensities‡, it was thought at first that such series might also exist in neon, and as two of the helium series consisted of doublets, it was hoped that the detection of similar doublets in neon might indicate lines which belonged to the same series. In the case of helium the constant oscillation frequency difference between members of a pair is 1·00, and consequently, if this difference is proportional to the square of the atomic weight, the corresponding value for neon might be about 25. Now there is, as it happens, an unusually large number of oscillation frequency differences between 25 and 26, but the total number is only 13, and there appears to be no connexion between the intensities of the pairs of lines. Consequently, this hypothesis was, for the time being, abandoned.

The next step was to plot the positions and relative intensities of all the lines on a large scale, and an examination of the map of the spectrum thus produced showed that the lines appeared to be

* *Roy. Soc. Proc.* A. Vol. LXXXI. 1908, p. 181.
† *Phil. Trans.* A. Vol. CCII. 1903, p. 183.
‡ Runge and Paschen, *Astrophys. Journ.* Vol. IV. 1896, p. 91.

divided into three groups with considerable gaps between them. The first of these groups extends from the extreme red to λ4071, and consists of a great mass of lines, 252 in all, among which are many weak ones, especially at the blue end. The second group extends from λ3754 to λ3370, and contains 29 lines only, but all of these with the exception of 5 very weak and doubtful ones, are of considerable strength. The third group reaches from λ3167 to λ2736, there being 40 lines in all, though a subdivision is possible owing to the fact that there is an obvious gap between λ2911 and λ2872. Also the lines on the less refrangible side of this gap are considerably stronger than those on the other, and among the former, no very weak ones are to be found.

This arrangement suggested that the groups might be in some way repetitions of each other, that is to say, there might be constant frequency differences between certain corresponding lines in them, and consequently these differences were calculated between each line of the second group and all those of the third. The results were indefinite.

After this, the difference between each pair of lines in the second group was determined, and so also for the third group, and it was then found that a distinct regularity existed, inasmuch as many of the lines could be grouped into triplets with constant frequency differences, the difference between the first and second lines being approximately 1429, and that between the first and third 1847. A search was then made in the rest of the spectrum for more of these triplets, and several were found in the extreme red, but no others seemed to exist. There were, it is true, several other pairs of lines with one of the above differences between them, but this is to be expected from considerations of probability, and in no case was the triplet complete.

In addition, on examining the second group, it was found that there were three pairs of lines with a frequency difference of 1070, the first line in each case being the first member of a triplet. In view of the small number of lines in this group this could hardly be accidental, especially as three similar pairs occurred in the third group, and three in the first, and the difference in question did not appear again. It seems, therefore, that in the whole spectrum there are nine quadruplets, and a number of triplets with the same frequency differences, but with the second line absent. Moreover, it was found that these triplets and quadruplets were not merely groups of three or four lines occurring among a number of others, but that practically all the lines in certain regions of the spectrum were capable of arrangement into such groups. Thus, in the second large division of the spectrum which practically consists of 24 bright lines, there are three quadruplets and four triplets, in one of each of which a line is missing, and only two lines do not

fit into the scheme. The first of these is the strongest line in the whole group, and the second one is brighter than nearly all the others. In the third group, or rather in the first subdivision of it previously mentioned, there are also only two lines which are not members of triplets or quadruplets, while all the rest, 25 in number, fall into these natural groups. It is interesting to note, however, that one line, λ2992, occurs twice. Also, the members of the last two quadruplets are so close together that they appear to have been resolved only in two cases. When the wave lengths were first published, the line λ2949 was marked "broad," and is doubtless double, a fact which is also indicated by the abnormal frequency difference, and it is quite possible that the line λ2913 is double as well.

On turning to the first group of lines, it is found that not all of them belong to triplets or quadruplets, although most of the stronger ones do. It must be remembered, however, that the numbers representing the intensity according to the usual convention merely indicate which lines are brighter than others, and which are of approximately equal intensity. Actually, the energy corresponding to a line of intensity 10 is probably many thousand times that of one of intensity 1, and this difference is very apparent on visual observation, especially in the case of the present spectrum, for on looking at the region in which the regularities occur with an ordinary spectroscope, 23 very bright lines are seen and no others, unless special precautions are taken. Of these lines, all are members of triplets or quadruplets except two, λ6402 and λ6074. In addition, the former is the brightest line between the wave lengths under consideration. It is also interesting to note that if the pressure of the gas is fairly high, say above 5 mm., these 23 lines and two others, λ7245 and λ5852, constitute practically the whole of the visible spectrum, and it is remarkable that the latter line, which is the brightest in the entire spectrum, is just outside the region of triplets and quadruplets, and does not take part in their composition. It may also be mentioned that while examining these bright lines with a constant deviation Hilger spectroscope, an additional very weak one was observed in the extreme red, the wave length as given by the instrument being about λ7445.

The following tables show how the lines have been arranged.

In column 1 is given the oscillation frequency *in vacuo* of the first line, followed by its wave length in air and its intensity. The fourth column shows the difference between the *oscillation frequencies* of the first and second line, the wave length and intensity of which follow. The next column gives the difference between the oscillation frequencies of the first and third lines, and so on. The actual oscillation frequencies are not given except for the first line, but of course may be calculated from the differences.

$10^8/\lambda$	λ	Int.	Diff.	λ	Int.	Diff.	λ	Int.	Diff.	λ	Int.
14232·22	7024·38	2	1070·33	6533·08	6	1429·78	6383·14	9	1847·20	6217·44	6
14883·08	6717·22	7	1069·97	6266·69	6	1429·34	6128·63	5	1846·62	5975·76	5
15149·28	6599·18	9	1070·24	6163·73	6	1429·41	6030·20	5	1846·95	5882·06	5
26628·6	3754·32	3	1069·7	3609·33	3	—	—	—	1846·4	3510·87	4
27767·6	3600·32	6	1070·2	3466·70	5	1429·1	3424·08	3	1847·3	3375·74	2
27818·8	3593·69	8	1069·7	3460·61	5	1429·6	3418·03	5	1846·3	3370·02	5
31560·6	3167·62	2	1069·0	3063·83	2	1428·5	3030·44	2	1846·0	2992·57	3
32465·7	3079·31	1	1070·0	2981·06	1	1430·8	2949·32	1	1847·1	2913·28	2
32468·7	3079·02	1	1069·8	2980·81	1	1427·8					
						Triplets					
13934·95	7174·25	2				1429·67	6506·69	9	1846·96	6334·65	9
14426·56	6929·78	6				1429·64	6304·97	6	1846·89	6143·31	7
14969·37	6678·50	9				1429·40	6096·36	6	1846·85	5945·02	6
27009·9	3701·31	5				1429·1	3515·32	5	1846·6	3464·46	4
27123·2	3685·86	4				1429·3	3501·34	5	1847·4	3450·88	4
27148·9	3682·37	4				1429·4	3498·19	5	1846·8	3447·83	5
27511·8	3633·80	5				1429·5	3454·31	5	—	—	—
31701·7	3153·51	2				1429·3	3017·47	3	1846·6	2979·94	2
31750·2	3148·70	2				1429·0	3013·09	3	1846·4	2975·65	1
31759·0	3147·82	1				1429·4	3012·25	3	1846·2	2974·89	3
31977·4	3126·33	2				1429·2	? 2992·57	3	—	—	—
32489·2	3077·08	2				1428·9	2947·44	3	1847·0	2911·55	1
32697·2	3057·51	3				1429·0	2929·47	1	—	—	—

With regard to the agreement between the different values for the constant frequency differences, it may be noted that if the error in the wave length of a single line is 0·03, that of the difference of two may be 0·06, and the maximum variation is 0·12. This, in the scale of oscillation frequencies corresponds roughly to 0·3 for the first group of lines, and 1·0 for the other two, and it will be observed that this limit is rarely exceeded, though it may be remarked that the actual values of the differences in the first group seem slightly larger than the others, and also that those between the triplets are more constant than those between the quadruplets; possibly the lines composing the former are slightly sharper than the others, although no actual difference is apparent. The author's values for the wave lengths and intensities have been used throughout, as Baly's figures, though possibly rather more accurate, are not complete.

There appears to be no very definite relation between the intensities. Generally speaking, the lines in the first group are brighter than those in the second, and these in turn brighter than those in the third. Also, corresponding lines in the same group have often the same intensities, this being especially well marked in the case of the triplets. The figures representing the intensities in the extreme red are probably far too small, as they show only the extent to which a photographic plate is affected, and in this portion of the spectrum, the total energy is, no doubt, considerably greater than that indicated in this way.

It is not proposed to discuss fully a number of interesting points which are raised by the existence of these regularities. The main facts so far ascertained may, however, be outlined. Firstly, if the bright lines only are considered, the spectrum falls naturally into three groups of lines which diminish in general intensity on approaching the ultra-violet end. The first group consists of one very bright line, one weaker line, three quadruplets and three triplets; the second of one very bright line, one weaker line, three quadruplets and four triplets; while the third group contains also two bright lines, three quadruplets, and six, or possibly only five, triplets.

This arrangement naturally suggests a principal series and two subordinate ones, the second, or both of the latter, consisting of triplets or quadruplets, or possibly a principal and two subordinate series of quadruplets alone, and others of triplets alone, especially as a grouping in threes seems to predominate; but even if some such connexion does exist, it would be exceedingly difficult to determine, since there are at present only three members of each series.

The whole arrangement also strikingly resembles the blue portion of the red argon spectrum investigated by Rydberg*.

* *Astrophys. Journ.* Vol. VI. 1897, p. 338.

This author found that all the lines between certain limits except a few very weak and doubtful ones, could be arranged in a scheme of 7 quadruplets, 6 triplets, and 10 doublets, in a very similar manner to the neon lines above, but the mean frequency differences from the first line were in this case 846·5, 1649·7 and 2256·7. Two lines, however, were not included, and one of these was the brightest of all those under consideration. It seems hardly possible that such a coincidence can be accidental.

With regard to the other and weaker lines of the spectrum, which consist of a number in the first group, and all those in the second subdivision of the third group, a regularity is not at present apparent. A partial search has so far failed to reveal any constant frequency differences, but it by no means excludes their existence. As, however, there are in all some 25,000 differences, the work is necessarily slow. Another possibility is that these lines are the components of a number of series similar to those in helium, a supposition which is strengthened by the fact that there are a great many weak lines close together at the blue end of the first group. From the point of view of intensity alone, this portion of the spectrum is somewhat analogous to the secondary spectrum of hydrogen, and while there can be no doubt that there is some relation between the lines composing it, the solution of the problem is not easy. The investigation of these lines and of the brighter ones is being continued, and it is hoped that by means of methods which are not solely mathematical, some further light may be thrown on the true constitution of this remarkable spectrum.

The Intensity of Secondary Homogeneous Röntgen Radiation from Compounds. By J. C. CHAPMAN, B.Sc., Layton Research Scholar of the University of London (King's College), Research Student of Gonville and Caius College, Cambridge, and E. D. GUEST, B.A., formerly Scholar of Exeter College, Oxford. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 13 March 1911.]

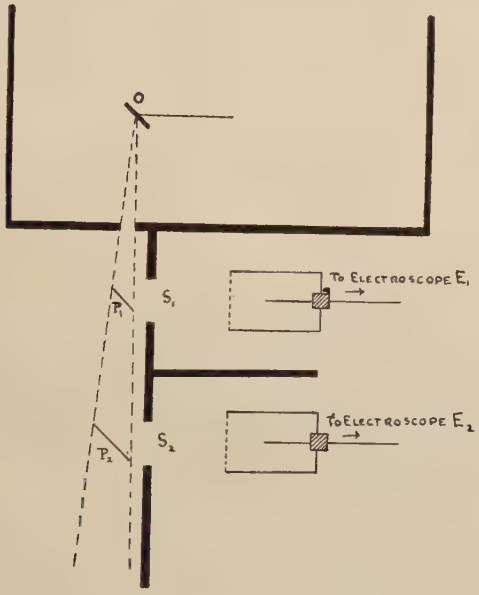
Of the two types of secondary radiation emitted by elements of atomic weights between chromium and iodine, it has been shown that one is a scattered radiation having the same penetrating power as the primary beam and resembling it in that it is heterogeneous*, and the other an X-radiation characteristic only of the element emitting it, the penetrating power of which is independent of the penetrating power of the primary beam†. The former type of radiation has been explained on the assumption that the electrons are accelerated by the electric forces in the primary pulses‡. In the case of the elements with the range of atomic weights above mentioned it is well known that the scattering effects are small.

Numerous experimenters have shown that the type of this characteristic secondary X-radiation is not affected by the state of chemical combination of the element and this holds also when there is a change in the valency of the metal in the compound. So far all these experiments have been qualitative in their nature, the object of this research was to investigate quantitatively the secondary homogeneous X-radiation emitted from elements when combined in different compounds. In the first experiment strontium chloride was taken and then converted into strontium sulphate; and in the second experiment pure tin was first experimented upon and was then converted into tin nitrate.

The apparatus used is indicated in the diagram, X-rays leaving the anticathode O pass through two plates P_1, P_2. P_1 was very thin and produced the same type of secondary homogeneous radiation as the plate P_2. This radiation leaving P_1 passed through the slit S_1 into an ionization chamber connected to a Wilson tilted electroscope E_1. At the same time the rays emitted by the plate P_2 pass through the slit S_2 into a second ionization chamber connected to a tilted electroscope E_2. At right angles

* Barkla, *Phil. Mag.* June, 1906.
† Barkla and Sadler, *Phil. Mag.* Oct. 1908.
‡ *Conduction of Electricity through Gases*, 2nd edition.

to the main lead screen was placed a second screen, so that the electroscopes E_1 and E_2 were only affected by the rays coming from the plates P_1 and P_2 respectively. The object of the plate P_1 and the electroscope E_1 was merely to standardise the rays given off from the X-ray bulb. One of the difficulties in making these experiments to a sufficient degree of accuracy is that of the thickness of the plate P_2. If on the one hand the plate is not sufficiently thick it is difficult to measure the radiation emitted, and if on the other hand the plate is of moderate thickness this involves corrections for absorption inside the substance itself which owing to



their approximate nature must somewhat vitiate the results if they are of any great magnitude. This trouble was got over, however, by using a Wilson tilted electroscope and working in a moderately sensitive position, but in spite of using this electroscope the absorption by the thinnest plates, which it would be possible to work with in the case of elements of low atomic weights, would be too great to yield accurate results after the more or less doubtful corrections for absorption had been made.

Experiments with Strontium.

In order to get a sufficiently thin layer of the salt, a dilute solution of strontium chloride was evaporated slowly to dryness in a very thin aluminium tray approximately ·002 cm. in thick-

ness. This aluminium tray was then placed in a radiator stand made of thin aluminium and the intensity of secondary radiation emitted by the salt was measured. The plate P_1 consisted of a thin layer of strontium chloride, and this was kept in a fixed position throughout the experiment. The rates of deflection of the gold leaves were then observed concurrently in the two electroscopes. Owing to the small quantity of salt which it was found advisable to use, the radiation from the air, the radiator stand, and the tray in the absence of the strontium was first determined, and the increase when the salt was deposited on the tray served to measure the intensity of secondary homogeneous radiation emitted by the salt. The purely scattered radiation from such compounds has been shown by numerous experimenters to be exceedingly small.

The aluminium tray containing strontium chloride was then removed and the latter was converted into strontium sulphate by the addition of dilute sulphuric acid and by slowly evaporating again a layer was obtained. The salt was then replaced in the fixed stand and the same process was repeated as in the former case.

In order to make as accurate a correction as possible the normal absorptions of the strontium chloride and the strontium sulphate for an homogeneous strontium radiation were determined. These it will be seen are very small, so that any error in the approximations which is made will only affect the result to a very small extent. In order to make clear the order of magnitude of the error resulting from these approximations the correction for strontium is worked out in full.

Strontium.

The intensities given correspond to a definite intensity of primary beam as measured by the standardising electroscope.

Homogeneous radiation from strontium when in form of strontium chloride and scattered radiation from stand, air, etc.	24·7
Homogeneous radiation from strontium when in form of strontium sulphate and scattered radiation from stand, air, etc.	24·1
Scattered radiation from stand, air and aluminium tray	16·4

Hence

Homogeneous radiation from strontium when in form of strontium chloride	8·3
Homogeneous radiation from strontium when in form of strontium sulphate	7·7

Absorption of strontium homogeneous radiation when passing normally through strontium chloride ...	1·96 °/₀
Absorption of strontium homogeneous radiation when passing normally through strontium sulphate ...	4·0 °/₀

Owing to the obliquity of the radiating layer with reference to the ionization chamber the effective thickness of the layer was greater than for that involved in normal absorption. This change in effective thickness is easily calculated. The orientation of the plate being known it was possible to calculate the difference from ordinary geometrical considerations. The effective thickness worked out in this case to be 1·22 the normal thickness. The absorption was found experimentally when the layer was normal to the radiation, and as the correction for absorption was small it was assumed that the absorption for a layer of effective thickness 1·22 times this normal thickness of the layer was 1·22 times this absorption found by experiment.

There is one other point to be noticed with regard to the corrections for absorption. The secondary homogeneous radiation does not pass through the whole layer, it is produced in this layer so that some of it will pass through only a small part of the thickness while some will pass through the greater part of it. Owing to the smallness of the absorption this was allowed for by taking the correction to be one-half the calculated correction in the case of all the radiation passing through the whole layer.

Absorption of strontium homogeneous radiation when passing normally through strontium chloride . 1·96 °/₀
Multiplying this percentage by 1·22 to allow for the orientation of the layer . . . . . 2·4 °/₀
Halving this, 1·2 °/₀ is the calculated correction to apply.
Adding 1·2 °/₀ to 8·3 we have 8·4 instead of 8·3 for the chloride.

Similarly in the case of strontium sulphate

$$4{\cdot}0 \times 1{\cdot}22 = 4{\cdot}9,$$

and half this is 2·4.

Adding 2·4 °/₀ to 7·7 we have 7·9 instead of 7·7 for the sulphate. Thus

$$\frac{\text{Intensity of secondary homogeneous radiation from the strontium in the form of strontium chloride}}{\text{Intensity of secondary homogeneous radiation from the strontium in the form of strontium sulphate}} = \frac{8{\cdot}4}{7{\cdot}9} = 1{\cdot}06.$$

The above results show to within the errors of experiment that the strontium atoms emit the same intensity of secondary homogeneous radiation whether combined in the sulphate or chloride compound.

Experiments with Tin.

In this case the characteristic radiation from the pure metal was first examined. The tin was then converted into tin nitrate and its radiation again examined. It may be added that in the case of the tin only the harder type of radiation was measured since there was in front of the ionization chamber a sheet of aluminium of sufficient thickness to cut off all the softer rays. As before, the percentage absorptions of the tin and tin nitrate for homogeneous tin radiation were measured.

Throughout the experiments both with the strontium and with the tin the X-ray bulb was kept hard so that the incident primary beam and any scattered radiation from the aluminium stand, etc., should not be absorbed appreciably by the thin layer of salt.

Tin.

As before the intensities given correspond to a definite intensity of primary beam as measured by the standardizing electroscope.

Homogeneous radiation from tin when in uncombined state and scattered radiation from stand, air, etc. ...	12·7
Homogeneous radiation from tin when combined as tin nitrate and scattered radiation from stand, air, etc. ...	12·8
Scattered radiation from stand, air and aluminium tray	6·5

Hence

Homogeneous radiation from tin in uncombined state ...	6·2
Homogeneous radiation from tin in combined state ...	6·3

Absorption of tin homogeneous radiation when passing normally through uncombined tin	4·4 %
Absorption of tin homogeneous radiation when passing normally through layer of tin nitrate	5·9 %

Applying correction for absorption inside the substance itself as in the case of strontium previously given the above values give:

$$\frac{\text{Intensity of secondary homogeneous radiation from the tin in the form of tin nitrate}}{\text{Intensity of secondary homogeneous radiation from the tin in the uncombined state}} = 1{\cdot}03.$$

These results clearly indicate that whether the metal is combined or not, or whatever its compound, the intensity of secondary homogeneous radiation depends merely upon the quantity of the emitting element present; in other words, secondary homogeneous radiation is a purely atomic phenomenon.

Incidentally these experiments throw an interesting light on the method of production of this particular type of radiation. In previous papers by one* of us arguments have been advanced pointing to the fact that the characteristic secondary radiation does not result from the subsequent bombardment of atoms by ejected electrons. In the case of the experiment with the pure tin the ejected electrons are almost wholly absorbed by the tin atoms whereas when the tin is in the form of tin nitrate a considerable portion of the ejected electrons must be absorbed by the nitrogen and oxygen atoms, so that if this subsequent bombardment were an explanation quite a measurable difference should be observed in the intensities of radiation emitted in the two cases. The experiments, however, show that this is not the case.

In conclusion, our best thanks are due to Professor Sir J. J. Thomson for his kind interest in these experiments.

* Chapman and Piper, *Phil. Mag.* June, 1910, and Chapman, *ibid.* April, 1911.

An Attempt to detect a Fatigue Effect in the production of Secondary Röntgen Radiations. By J. Crosby Chapman, B.Sc., Layton Research Scholar of the University of London (King's College), Research Student of Gonville and Caius College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 13 March 1911.]

More* has made experiments on the subject of the fatigue of metals as regards the production of secondary Röntgen radiations. He obtained small positive results with iron, lead, zinc and nickel. Gowdy† has continued this work, using more delicate methods. His experiments were made both on purely scattered radiation given by a substance such as aluminium and the characteristic homogeneous radiation emitted by elements in the group of substances with atomic weights between those of chromium and iodine. In the case of these elements it may be said, however, that scattering is present but is very small when compared with the intensity of the homogeneous radiation, so that any experiments made with such elements as radiators deal almost wholly with characteristic radiation, while with aluminium as radiator it is wholly the scattered radiation which is concerned.

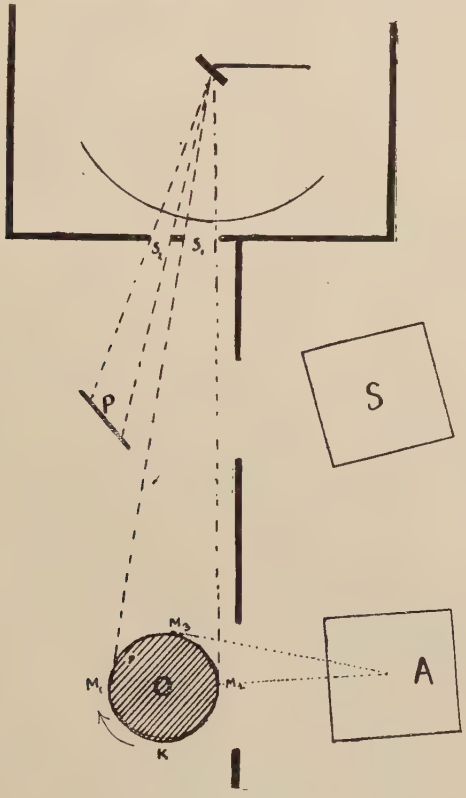
The results given in Gowdy's paper indicate that there is a fatigue in the power of producing secondary radiations in most metals of the order of 1% approx. after an exposure of one, two or three hours.—He mentions, however, that with aluminium he could detect no fatigue effect.—These alterations in the radiating power of the metals when exposed to an exciting beam of X-rays are probably explained as due to oxidation, for while five out of the seven metals he first tested exhibited variations in radiating power, of the thirteen oxidised surfaces afterwards used not one showed traces of fatigue. In addition the seven oxidisable metals which he experimented with all fatigued when exposed to ozone. So that his results seem rather to be of a chemical nature than what may be called a true fatigue.

Gowdy's method consisted in first comparing the initial radiating powers of the standardising and trial plates. The standardising plate was then shielded while the trial plate was exposed for several hours. The shield was then removed and the radiating powers of the two plates again measured by a balancing method. Such an arrangement, however, only serves to detect fatigues which last, at any rate, over an appreciable fraction of the time spent in comparing the efficiency of the two radiators. Thus

* More, *Phil. Mag.* Vol. xiii. 1907, p. 708.
† Gowdy, *Phys. Rev.* Vol. xxx. 1910, p. 62.

assuming there to be a fatigue effect lasting $\frac{1}{10}$th sec. it would not have been noticed using this apparatus.

It would seem, however, much more likely that any genuine fatigue of the plate would last only for very short periods of a second, and with the idea of detecting such short periods of fatigue the following apparatus was used.



Apparatus.

Beams from an X-ray bulb passed through the two slits S_1 and S_2 in the lead box and fell upon a metal cylinder O and a plate P respectively. This cylinder, mounted on ball-bearings, was driven by a motor about a vertical axis and was capable of high speeds of revolution. The cylinder served as the secondary radiator, the fatigue of which was to be measured, while the plate P merely standardised the variable X-ray bulb. Secondary radiation leaving the plate P passed into the standardising electroscope S and the radiation from the cylinder O entered the electroscope A at the same time.

If the X-ray tube is working and the cylinder is made to rotate, then tracing out the path of any portion of the cylinder it can be divided into three distinct parts, for while moving

(1) from M_2 through K to M_1 there is no exposure to X-rays;

(2) from M_1 to M_3 there is exposure to X-rays but no secondary rays can pass from that portion to the electroscope A;

(3) from M_3 to M_2 there is both exposure to X-rays and the particular portion of the cylinder is in a position to send secondary rays to the measuring electroscope.

Experiments on Fatigue with the Secondary Homogeneous Radiations from Zinc and Copper.

The cylinder (5 cms. in diameter and 6 cms. high) was made of brass and the standardising plate of the same material.

Suppose now the cylinder to rotate in the direction of the arrow, that is clockwise. A particular portion of the cylinder coming to the point M_3, after which it can send rays to the electroscope A, has just previously been excited over the period of time occupied in travelling from M_1 to M_3. Now from other results it can be shown that the cylinder in this time was able to reach a steady radiating state. This was proved by rotating the cylinder in an anti-clockwise direction. It was found then that the intensity of radiation reaching the electroscope A was the same when the cylinder was rotating anti-clockwise as when at rest.

Speed no. of revolutions	Intensity of sec. radn. when rotating at speed in col. 1	Intensity when stationary	Intensity when stationary / Intensity when rotating
60	44·9	45·0	1·00
60	29·7	29·3	1·01
60	29·8	29·8	1·00
60	30·5	29·9	·98

This showed that any particular portion of the radiator while passing from M_2 to M_3 had time to take up a steady radiating state. Now the $\angle M_2 OM_3$ is slightly greater than $\angle M_1 OM_3$. We are therefore justified in assuming that the part of the cylinder reaching M_3 when rotating clockwise was in a *constant* stimulated state. It appeared possible therefore that a great many of the atomic systems in a condition to give out the high-speed electron and thus cause the homogeneous radiation might have been used up, so that on reaching the neighbourhood M_3M_2 the particular

part of the cylinder (which has passed through $M_1 M_3$) would not be so efficient in producing radiation as if just before arriving at $M_3 M_2$ it had not been excited by the X-rays. Consider now the effect of a rotation in the opposite direction (counter-clockwise). In this case the part of the cylinder coming into the region of excitement $M_2 M_3$ has just previously had a complete rest over the time spent in travelling from M_1 through K to M_2. So that if there is a fatigue effect extending over these range of times the intensity of radiation passing into the electroscope A will depend on the direction of rotation of the cylinder.

This is the basis of the method employed. The cylinder was first rotated in a clockwise direction. The X-rays were switched on and the deflection in the electroscope A while the standardising electroscope underwent a certain deflection was observed. The cylinder was then made to rotate in the opposite direction and the deflection in A again measured while the leaf in S was deflected to the same extent as previously.

Revolutions per sec. made by cylinder	A. Intensity of radiation from cylinder when rotating clockwise	B. Intensity of radiation from cylinder when anti-clockwise	Ratio $\frac{A}{B}$
60	64·2	63·9	1·005
60	63·7	63·3	1·006
60	62·9	63·0	1·000
60	63·3	63·9	·994
60	63·9	63·8	1·000
60	63·9	64·0	1·000
60	65·0	65·3	·996
60	63·9	64·0	1·000
60	63·9	63·8	1·000
60	63·6	63·6	1·000

$$\text{Mean ratio } \frac{\text{Intensity of radiation when clockwise rot.}}{\text{Intensity of radiation when anti-clockwise rot.}} = 1{\cdot}001.$$

Now the time spent in passing from M_2 to M_3 is approximately equal to $\frac{1}{300}$th sec.

That is if the radiator is fully excited and has reached a steady state and then its power of emitting secondary homogeneous radiation is compared (by a method which only allows time of the order of $\frac{1}{600}$th sec. for recovery) with that of a radiator not previously excited, the results indicate that there is no alteration in the two powers of emitting radiation.

It was thought desirable to see if any fatigue was present in the case of a metal which gave a purely scattered radiation. *A*

priori reasoning, though, would certainly suggest that the possibility of detection with this radiation is much less than with the homogeneous type. For in this case after an atom has served as the source of the Röntgen rays it is not left in the peculiar condition of having lost an electron as it is when emitting the characteristic rays.

Fatigue with Scattered Radiation.

The brass cylinder was replaced by one made of aluminium and care was taken to see that the primary rays from the X-ray box fell only on the aluminium and not on the brass base. The brass standardising plate was also removed and an aluminium plate substituted.

The same experiment was then repeated with the aluminium cylinder rotating first clockwise and then anti-clockwise, with the following results:

Revolutions per sec. made by cylinder	A. Intensity of radiation from cylinder when rotating clockwise	B. Intensity of radiation from cylinder when anti-clockwise	Ratio $\frac{A}{B}$
60	28·8	28·2	1·02
60	28·3	27·1	1·04
60	28·2	28·1	1·00
60	24·7	25·8	·96
60	22·1	22·0	1·00
60	22·4	22·7	·99
60	22·5	22·0	1·02
60	23·0	22·8	1·01
60	21·5	21·1	1·02
60	22·5	22·3	1·01
60	21·5	21·6	1·00

$$\text{Mean ratio } \frac{\text{Intensity of radiation when clockwise rot.}}{\text{Intensity of radiation when anti-clockwise rot.}} = 1{\cdot}006.$$

That is if the radiator is fully excited and has reached a steady state and then its power of emitting secondary scattered radiation is compared (by a method which only allows time of the order of $\frac{1}{600}$th sec. for recovery) with that of a radiator not previously excited, the results indicate that there is no alteration in the two powers of emitting radiation.

The interpretation of these results varies according as the radiation leaving the X-ray bulb is looked upon as a wave surface or a mere localisation of energy.

If the wave surface is assumed, it is evident that every atom would come under the action of the exciting beam; and in the case

of zinc and copper those that were in a suitable condition would eject a high-speed electron so that the results of the fatigue may be looked upon as showing that these atoms with high-speed electrons are continually changing, giving place to fresh ones, or else that they themselves have a rapid time of recovery.

On the localisation of energy theory the fatigue would be quite impossible to detect, for after a particular atom is struck and presumably fatigued or ceased to act as a radiator the chance of its being struck again and acting as the source of radiation is in all probability infinitely small.

Persistence in the production of the Scattered Radiation.

Another point which enters into this experiment is the persistence effect in the production of the homogeneous and scattered radiations. That is to say, the continuation of the emission of the radiation by an atom after the removal of the exciting beam. In a previous paper* it was shown that whatever the effect inside the atom may be, it is in the case of the homogeneous characteristic radiation from zinc and copper rapidly damped and cannot continue in sufficient strength to give $\frac{1}{200}$th of the original secondary radiation after a period of $\frac{1}{3000}$th sec. This result was obtained when dealing with the characteristic radiations. The experiments made when using the aluminium cylinder incidentally show that there is no persistence effect in the purely scattered radiation from aluminium.

For suppose this continuation of emission does take place the preceding observations would have detected it. Assuming the cylinder to be rotating in a clockwise direction, then when a particular portion of it passes from the field of excitement $M_3 M_2$ if it still continues to emit X-rays they will pass into electroscope A, whereas with a rotation in an opposite direction any persistence which occurs will take place after leaving M_1, and thus it will not have any effect on the electroscope A. In this manner then only in the first case should there be an increase in the radiation reaching the electroscope.

The results given above for the aluminium cylinder show that within the limits of experimental error no such effect can be detected, and working out the results more in detail the following conclusion is reached. The vibrating system causing the scattered radiation is very rapidly damped and does not continue in sufficient strength to emit $\frac{1}{50}$th of the original radiation after a period of $\frac{1}{3500}$th sec.

I wish to express my thanks to Professor Sir J. J. Thomson for his interest and advice during this experiment.

* Chapman and Piper, *Phil. Mag.* June 1910.

On the Distribution of the Megapodidae in the Pacific. By J. J. Lister, M.A., St John's College.

[*Read* 6 February 1911.]

The genus *Megapodius* consists, according to M. Oustalet, of some nineteen species. The distribution of fifteen of these extends almost continuously from Borneo to the New Hebrides and from the Philippine Islands to Australia. It thus covers an area in which the land masses are nowhere very remote from one another. There are, however, four outlying species far removed from the rest of the genus, namely in Niuafou in the Tonga Group, the Pelew Islands, the Marianne Islands and the Nicobar Islands.

As the birds are incapable of long flight the question arises: How is the distribution of the outlying species to be accounted for? It has been suggested that it may indicate the existence of a former land area by which all these remote islands were at one time connected.

The object of this paper is to show that there is a good deal of evidence, negative and positive, to support the view that these outlying species may have reached their present habitats by the agency of the natives, by whom the eggs are highly valued as food.

Niuafou is an active volcano $3\frac{1}{2}$ miles in its longest diameter. The other birds inhabiting it are of species common to the Tonga Islands, though four, found in the other islands, are apparently absent from it. The birds are "protected" by the chief, and they exhibit a partial albinism though in very varying degrees. The native name for the bird is *Mallow*, identical with that of the Solomon Island species and with that generally used by Malay hunters throughout the East Indies. The nearest species of the genus (in distance, but not in affinities) is that of the New Hebrides, some 900 miles to the west, no megapode being known from the intervening Fiji Islands which consist of much larger and more ancient land masses.

With regard to the Pelew Islands, Semper gives evidence showing that they consist of raised coral rock investing a volcanic basis formed by a submarine eruption in late Tertiary time.

Quoy and Gaimard, the naturalists of the "Uranie," visited the Marianne Islands in 1819 and state that the species there found was domesticated by the natives.

M. Oustalet was inclined to include this bird and that from the Pelew Islands in one species, but Mr Ogilvie Grant regards them as distinct.

Wallace has expressed the opinion that the Nicobar bird has probably been introduced by the Malays.

There is evidence that the species found in the Solomon Islands exists in some places in a domesticated or semi-domesticated condition.

As the natives of the Pacific Islands were in the possession of fowls, dogs and pigs when they were first visited by Europeans the supposition that in some of their wanderings they may have carried megapodes with them, and thus established the outlying species in their present habitats, appears not improbable.

In support of this conclusion Professor J. Stanley Gardiner stated that the Sultan of the Maldive Islands, who died in 1878, had established megapodes on one of the islets of Male Atoll in that group. These had probably been obtained at the Nicobar Islands, between which and the Maldives there is regular trade communication.

The Production of Characteristic Röntgen Radiations. By R. WHIDDINGTON, B.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 29 March 1911.]

Introduction.

It is now well known that many elements when suitably stimulated can be made to emit secondary Röntgen rays of a type depending only on the element and not on the primary exciting rays. This kind of secondary radiation has been variously termed characteristic, homogeneous, or fluorescentradiation—it will be referred to below under the first name.

The most striking feature of a characteristic radiation (apart from its individuality) is that it can only be excited when the primary rays contain a constituent more penetrating than the characteristic itself.

The present research was entered upon with the object of defining that quality of primary radiation which *just* stimulates a characteristic in terms of the velocity of the cathode rays within the exciting Röntgen ray tube.

Put very briefly the method is as follows:—

A stream of cathode particles of known velocity was directed on to a suitable anti-cathode and the primary Röntgen rays so produced allowed to fall on a secondary radiator. As might have been expected no appreciable amount of secondary radiation was emitted from the secondary radiator until the velocity of the cathode particles within the tube exceeded a certain critical value, this value of course depending on the nature of the radiator.

The critical velocities for the radiators Cr, Fe, Ni, Cu, Zn, Se, have been determined with some accuracy; that for Al has been given in a paper not yet published* as $2{\cdot}1 \times 10^9$ cms./sec.

The apparatus.

The sort of apparatus used is shown in Fig. 1.

A parallel beam of cathode rays is directed from the cathode C down the tube L into the evacuated brass cylinder Z which is provided with four co-planer tubes, any one being at right-angles to its neighbour. The cylinder is wound on the outside with a

* *Nature*, Feb. 1911.

solenoid of thick copper wire so that when a current is sent round it a nearly uniform magnetic field is set up along the axis. Under such circumstances the heterogeneous beam of cathode rays from C is split up into a "spectrum," the individual rays traversing circles whose centres lie on the straight line MN.

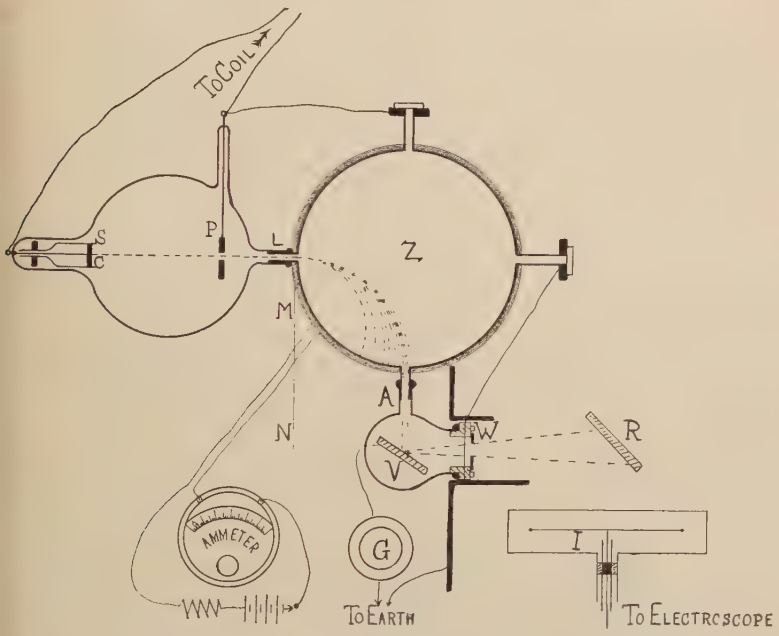


Fig. 1.

Thus with a certain current in the ammeter only rays of a definite known velocity can get through the tube A and fall on the anti-cathode V.

By converting the tube containing V into a Faraday cylinder connected through a galvanometer G to earth, the cathode ray current falling on V is also known.

The Röntgen rays pass out through the thin Al window W and fall on the secondary radiator R. The rays emitted by R are measured in the ionization chamber I in the usual way.

It is necessary to draw attention here to a device I have employed to alter the velocity of the cathode rays from C without having resource to the usual method of varying the gas-pressure.

Winkelmann* so early as 1900 showed that the smaller a cathode ray tube the harder it was at a definite pressure. The device indicated in Fig. 1 diminishes the effective size of the tube

* Winkelman, *Ann. d. Phys.* II. 4, 1900, p. 757.

without making any structural changes in the tube itself. The magnetically controlled sheath S determines by its position (at any definite gas-pressure) the velocity of the cathode rays emitted by C. Drawing out S hardens the tube, a linear connexion existing

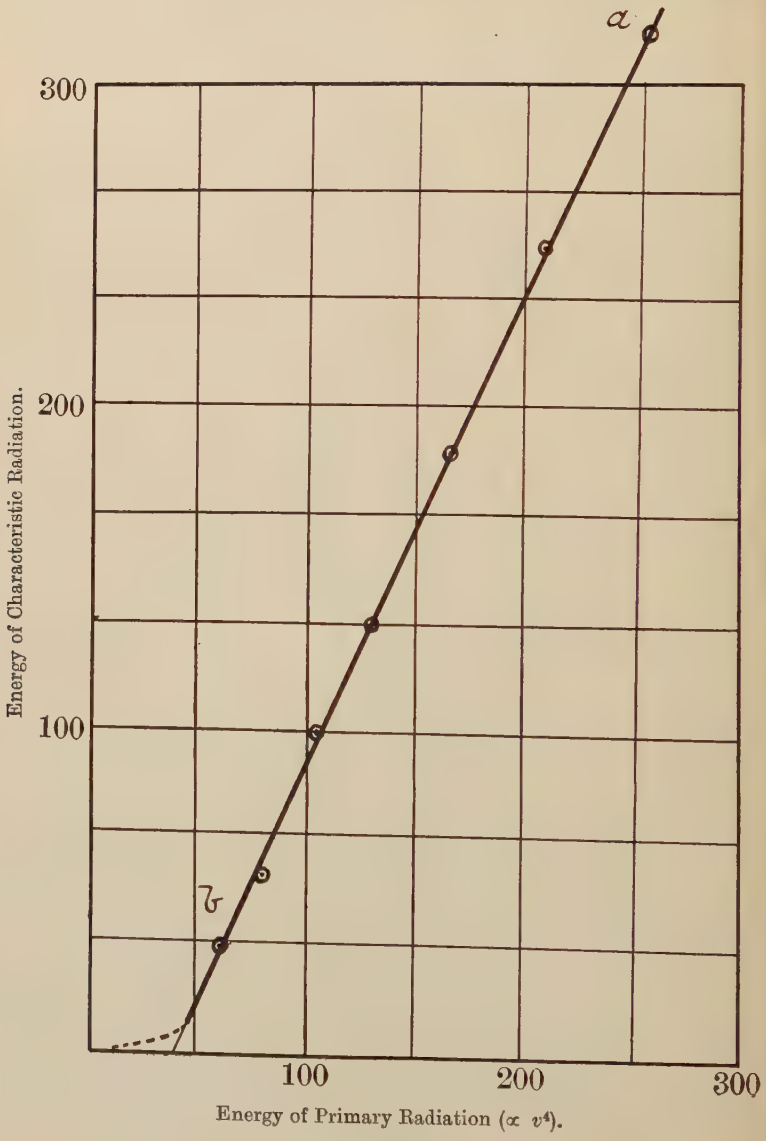


Fig. 2.

between the length of sheath drawn out and the potential at which the tube runs. This linear connexion only holds over a limited range however. This arrangement has been fitted to an otherwise ordinary focus-tube and works extremely well as an additional control on the hardness of the rays.

Experimental Results.

In all the experiments a silver anti-cathode was used.

The first experiments were carried out to find how the energy in the primary Röntgen rays depended on the velocity and number of the parent cathode rays.

Without giving details, the following two results have been obtained :—

(1) The Röntgen ray energy at any fixed velocity is proportional to the value of the cathode ray current, *i.e.* if the energy in the Röntgen rays emitted by n cathode rays is equal to E then the energy emitted by m particles is equal to $m/n \,.\, E$.

(2) The energy emitted by a cathode ray is proportional to the *fourth power* of its velocity*.

The first result is not surprising, while the second is interesting since the energy of the cathode rays themselves depends only on the square of their velocity.

The experiments with secondary radiators must now be mentioned.

In Fig. 2 is given a representative curve showing the connexion between E_s the energy in the secondary rays emitted from R and the energy (which is proportional to v^4) in the primary rays striking it. It is clear that a linear relation exists between the primary and secondary energies. The point at which the straight line *ab* (the curve is for a Cr radiator) cuts the x-axis gives approximately the above-mentioned critical velocity.

The following table gives the results for seven radiators including Al. For reasons which cannot be fully entered into here the value for Al given earlier as $2{\cdot}1 \times 10^9$ cms./sec. is altered to $2{\cdot}8 \times 10^9$ cms./sec. so as to bring Al into line with the other radiators in the table. This correction is desirable because Al does not appear to conform to the parallel of Stokes's Law which holds in the case of the other radiators.

Column 2 gives the potential in volts above which an X-ray tube supplied with a steady source of potential would have to run in order to excite the radiation characteristic of the element placed in the same line in Column 1. Column 3 gives the corresponding

* A result obtained from theoretical considerations by Sir J. J. Thomson in a paper on "The electrical origin of the radiation from hot bodies," *Phil. Mag.* Aug. 1907.

critical velocities of the radiating cathode rays. Column 4 gives the absorption coefficients in Al of the characteristic radiations concerned*. Column 5 gives the approximate atomic weight of the radiators.

Radiator	Potential	$v \times 10^{-9}$	λ/ρ	Atomic weight
Al	2600	2·8	580	27
Cr	7320	5·10	136	52
Fe	9200	5·70	88·5	56
Ni	10500	6·10	59·1	59
Cu	10800	6·18	47·7	63
Zn	11000	6·24	39·4	65
Se	14600	7·25	18·9	79

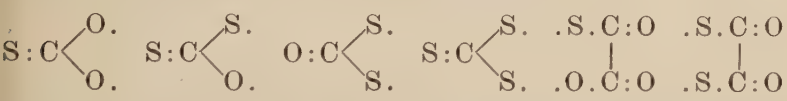
It is clear that for the range of experiments included in the table the critical velocity is proportional to the atomic weight of the radiator.

* Barkla and Sadler, *Phil. Mag.* 1908.

The Absorption Spectra of the Vapours of some Sulphur Compounds. By J. E. Purvis, M.A., St John's and Corpus Christi Colleges.

[*Read* 13 March 1911.]

The colour and absorption spectra of a number of sulpho-carbonates and sulpho-oxalates of various concentrations in absolute alcohol have been described by Purvis, Jones and Tasker*. Amongst other phenomena, it was shown that the replacement of oxygen by sulphur caused a considerable increase in the absorptive power of a compound which often results in the production of colour; and that definite absorption bands were shown by sulphur compounds possessing the following structures:—



The vapour of CS_2 has been shown by Pauer† to exhibit a series of 24 bands in the region of the spectrum between $\lambda 3300$ and $\lambda 2982$ when observed in a column 100 mm. long at 20° C. And when this substance was examined in an alcoholic solution represented by 1 in 200, there was a band ranging between $\lambda 3290$ to $\lambda 3000$; in a solution of 1 in 100, the band ranged between $\lambda 3330$ to $\lambda 2980$; and in a solution of 1 in 10, it ranged between $\lambda 3550$ to $\lambda 2750$.

The vapours of four of the sulphur compounds whose solutions were examined by Purvis, Jones and Tasker‡ have been investigated in order to ascertain if the single band exhibited by each of the solutions were resolved into a series of bands analogous to the phenomena observed by Pauer in the case of CS_2.

The author has described the detailed method employed in the study of other organic vapours§ and the same apparatus was used in the following experiments.

The substances whose vapours were examined were:—

Diethyl trithiocarbonate $CS(SC_2H_5)_2$,
Diethyl thionthiocarbonate $CS(OC_2H_5)(SC_2H_5)$,
Diethyl monothiooxalate $COSC_2H_5 . COOC_2H_5$ and
Dipropyl dithiooxalate $COSC_3H_7 . COSC_3H_7$.

* *Trans. Chem. Soc.* xcvii. 2287.
‡ *loc. cit.*
† *Wied. Ann.* lxi. 376.
§ *Trans. Chem. Soc.* xcvii. 692.

Diethyl trithiocarbonate $CS(SC_2H_5)_2$. The absorption band in the vapour of diethyl trithiocarbonate at various temperatures and pressures in a column 200 mm. long.

$t°$ C.	Pressure in mm.	
13	761	There was complete transmission of rays to λ 2270.
30	805	Rays transmitted to λ 2280; but weak between λ 3050 and λ 3000.
45	831	Rays only just visible between λ 3070 and λ 2980, and then they were transmitted to λ 2295.
60	861	The rays were absorbed between λ 3125 and λ 2875, and then transmitted to λ 2480.
75	891	The rays were absorbed between λ 3250 and λ 2780, and then transmitted to λ 2510.
90	921	The rays were absorbed between λ 3340 and λ 2690, and then transmitted to λ 2650.
100	937	There was complete general absorption from λ 3380.

These results indicate that the vapour exhibited one large band which became wider as the temperature and pressure were increased, and finally disappeared as a consequence of the overlapping general absorption.

The vapour of diethyl trithiocarbonate was also examined at a constant temperature of 17° C. and at different pressures. More of the vapour was introduced into the 200 mm. table than was used in the preceding observations, and the following table describes the observed phenomena at a constant temperature of 17° C. and at the noted ranging pressures:—

761 mm.	The rays were absorbed between λ 3320 and λ 2900, and were then transmitted to λ 2480.
631 mm.	The rays were absorbed between λ 3290 and λ 2910, and were then transmitted to λ 2380.
331 mm.	The rays were absorbed between λ 3290 and λ 2940, and were then transmitted to λ 2300.
31 mm.	The rays were absorbed between λ 3280 and λ 2950, and were then transmitted to λ 2290.

These numbers show that when more of the vapour was examined at a constant temperature and at different pressures only one large absorption band was observed which became narrower as the pressure was decreased.

Diethyl thionthiocarbonate $CS(OC_2H_5)(SC_2H_5)$. The absorption band in the vapour of diethyl thionthiocarbonate at various temperatures and pressures in a column 200 mm. long.

$t°$ C.	Pressure in mm.	
20	773	The rays were transmitted to λ 2300.
30	817	The rays were transmitted to λ 2480; but there was a considerable weakening of the rays between λ 3050 and λ 3000.
45	843	The rays were absorbed between λ 3070 and λ 2960, and then transmitted to λ 2480.
60	873	The rays were absorbed between λ 3120 and λ 2875, and then transmitted to λ 2480; the line λ 2480 being just visible.
75	903	The rays were absorbed between λ 3240 and λ 2795, and then transmitted to λ 2510.
90	933	The rays were absorbed between λ 3290 and λ 2700, and then transmitted to λ 2590.
100	949	The rays were completely absorbed from λ 3310.

These results show that the vapour exhibited a single large absorption band which became wider as the temperature and pressure were increased, and finally disappeared under the overlapping general absorption.

Diethyl monothiooxalate $COSC_2H_5.COOC_2H_5$. The absorption band in the vapour of diethyl monothiooxalate at various temperatures and pressures in a column 200 mm. long.

$t°$ C.	Pressure in mm.	
14	775	The rays were transmitted to λ 2295.
30	819	The rays were transmitted to λ 2320.
45	845	The rays were transmitted to λ 2380.
60	875	The rays were transmitted to λ 2480.
75	905	The rays were transmitted to λ 2520: but they were very weak between λ 3070 and λ 2980.
90	935	The rays were absorbed between λ 3120 and λ 2900, and were then transmitted to λ 2630.
100	951	The rays were absorbed between λ 3230 and λ 2810, and were then transmitted to λ 2640.

These results show that the vapour exhibited a single large absorption band which became wider as the temperature and pressure were increased. The band did not disappear as a

consequence of general absorption, and this can be accounted for by the fact that there was less vapour in the tube than in the preceding experiments.

Dipropyl dithiooxalate $COSC_3H_7 . COSC_3H_7$. The absorption band in the vapour of dipropyl dithiooxalate at various temperatures and pressures in a column 200 mm. long.

$t°$ C.	Pressure in mm.	
17	773	The rays were transmitted to λ 2295.
30	817	The rays were transmitted to λ 2295; but λ 2295 is much weaker than at 17° and 773 mm.
45	843	The rays were transmitted to λ 3315.
60	873	The rays were very weak between λ 3070 and λ 2980, and they were then transmitted to λ 2480.
75	903	The rays were absorbed between λ 3110 and λ 2900, and were then transmitted to λ 2480; the latter line was just visible.
90	933	The rays were absorbed between λ 3170 and λ 2820, and were then transmitted to λ 2583.
100	949	The rays were absorbed between λ 3240 and λ 2800, and were then transmitted to λ 2590.

These results show that the vapour exhibited one large absorption band which became wider as the temperature and pressure were increased. The band did not disappear as a consequence of general absorption, and this can also be accounted for by the fact that there was less vapour in the absorbing tube than is the case of diethyl trithiocarbonate and diethyl thionthiocarbonate.

General Results.

It is clear from the above observations that: (1) each of the vapours exhibits one large absorption band which widens as the temperature and pressure are increased; (2) the band is comparable with the band in the alcoholic solutions as described by Purvis, Jones and Tasker* except that the latter is shifted more towards the less refrangible regions of the spectrum as a result of the damping effect of the solvent on the vibrations or pulsations of the molecules; (3) there is no production of a series of narrow bands analogous to those observed by Pauer† in the vapour of CS_2; (4) the general absorption is shifted towards the less refrangible regions as the temperature and pressure are increased.

* *loc. cit.* † *loc. cit.*

With regard to the origin of the band, it is of some importance to recall the fact that open chain compounds do not, as a rule, exhibit absorption bands; and it is suggested that the origin of the band of the described substances may be explained from a consideration of the orientation of the —CO groups and the sulphur atoms as a closed chain. For example, on this hypothesis the formula of dipropyl dithiooxalate would be:—

$$\begin{matrix} C_3H_7.S—CO \\ \| \quad | \\ C_3H_7.S—CO \end{matrix}$$ derived from an acid whose formula would be $$\begin{matrix} H.S—CO \\ \| \quad | \\ H.S—CO \end{matrix}$$

And when one of the sulphur atoms in the fundamental ring

$$\begin{matrix} .S—CO \\ \| \quad | \\ .S—CO \end{matrix}$$

is replaced by tetravalent oxygen, the formula of diethyl monothiooxalate would be:—

$$\begin{matrix} C_2H_5.S—CO \\ \| \quad | \\ C_2H_5.O—CO \end{matrix}$$ derived from an acid whose formula would be $$\begin{matrix} H.S—CO \\ \| \quad | \\ H.O—CO \end{matrix}$$

In the latter case, the maximum valency of oxygen comes into action as indicated by the graphic formula.

A similar explanation may account for the band observed in the thiocarbonates. The fundamental closed chain in the case of these compounds would be:—

$$\begin{matrix} .S \\ \| \\ .S \end{matrix} \!\!> CS,$$

and the formula of diethyl trithiocarbonate on this hypothesis would be written graphically as:—

$$\begin{matrix} C_2H_5.S \\ \| \\ C_2H_5.S \end{matrix} \!\!> CS,$$ derived from an acid whose formula would be $$\begin{matrix} H.S \\ \| \\ H.S \end{matrix} \!\!> CS$$

When one of the sulphur atoms of the ring is replaced by tetravalent oxygen, diethyl thionthiocarbonate is produced whose formula would be:—

$$\begin{matrix} C_2H_5.S \\ \| \\ C_2H_5.O \end{matrix} \!\!> CS,$$ derived from an acid whose formula would be $$\begin{matrix} H.S \\ \| \\ H.O \end{matrix} \!\!> CS$$

It is also to be noticed that the band of diethyl thionthiocarbonate at 90° C. and 933 mm. pressure is not so wide as that of diethyl trithiocarbonate at 90° C. and 921 mm. pressure; for a difference of 12 mm. pressure would hardly account for a difference

of 260 Ångström units in the width of the bands. Similarly, the band of diethyl monothiooxalate at 100° C. and 951 mm. pressure is not so wide as that of dipropyl dithiooxalate at 100° C. and 949 mm. pressure. These differences may be caused by the lessened elasticity of the closed rings produced by a diminution in the attractive force of the sulphur and oxygen atoms when one sulphur atom is replaced by one atom of oxygen, and on the assumption of its quadrivalent valency by the oxygen in the formation of the rings. In connexion with this line of argument, it may be mentioned that in the solutions of these compounds, the absorption bands described by Purvis, Jones and Tasker (*loc. cit.*) almost disappear when the aliphatic groups are replaced by phenyl groups; and on the above hypothesis, the explanation of the phenomena is that the heavier aromatic residues damp still further the oscillations or rhythmical pulsations of the rings concerned with the absorption of light and so that less light is absorbed.

I have again to thank the Government Grant Committee of the Royal Society by whose assistance the spectroscope used in this and other investigations was purchased.

On the Scattering of Röntgen Radiation. By E. A. Owen, B.Sc. (Wales), 1851 Exhibition Scholar, Trinity College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 20 February 1911.]

When X-rays fall on a thin radiator, it was found by Bragg and Glasson* that a want of symmetry is shown by the secondary rays—the intensity on the emergent side being greater than on the incident side. It was also observed that the dissymmetry depended upon three factors, (*a*) the nature of the radiator, (*b*) the thickness of the radiator and (*c*) the state of the bulb, but to a greater extent on (*a*) than on either (*b*) or (*c*). Barkla† and Crowther‡ have examined the distribution of the scattered secondary radiation round a radiator; the former finds that a dissymmetry is exhibited when we get near the primary, whilst the latter finds that the dissymmetry is shown at all angles with the primary, increasing as we get nearer to it.

The following experiment was carried on simultaneously with the experiments of Barkla and Crowther. The distribution of the scattered secondary radiation round a radiator was investigated and, in addition, the variation of this distribution with (*a*) the hardness of the primary beam, and (*b*) the thickness of the radiator.

We can easily find what distribution to expect on the aether pulse theory. On this theory the X-ray is a pulse in the aether caused by the sudden stoppage of a cathode particle, this pulse being the seat of very intense electric and magnetic forces.

Let us consider a beam of X-rays falling normally on a thin radiator whose absorption is negligible. Suppose E is the average electric intensity in the different pulses in this beam.

Take a pulse in which the electric force is in a direction making an angle θ with the horizontal axis OX in the plane of the radiator. (See Fig. 1).

The components of electric force in two directions at right angles to each other in a plane, which is normal to any direction OP making an angle ϕ with the normal to the radiator, and in the horizontal plane ZOX, are $E \sin\theta$ and $E \cos\theta \cos\phi$.

$\therefore$ Energy of secondary pulse along OP

$$\propto E^2 \sin^2\theta + E^2 \cos^2\phi \cos^2\theta$$

$$\propto E^2 (1 - \cos^2\theta \,.\, \sin^2\phi).$$

* Bragg and Glasson, *Phil. Mag.* June, 1909.
† Barkla, *Phil. Mag.* February, 1911.
‡ Crowther, *Proc. Camb. Phil. Soc.* xvi. 1911, p. 112.

This gives the contribution to the energy of the secondary pulse along OP due to the primary pulse whose electric intensity makes an angle θ with OX.

$\therefore$ Total energy of secondary rays along OP

$$= K\int_0^{2\pi} (1 - \cos^2\theta \sin^2\phi)\, d\theta$$
$$= K'(1 + \cos^2\phi) = I_\phi.$$

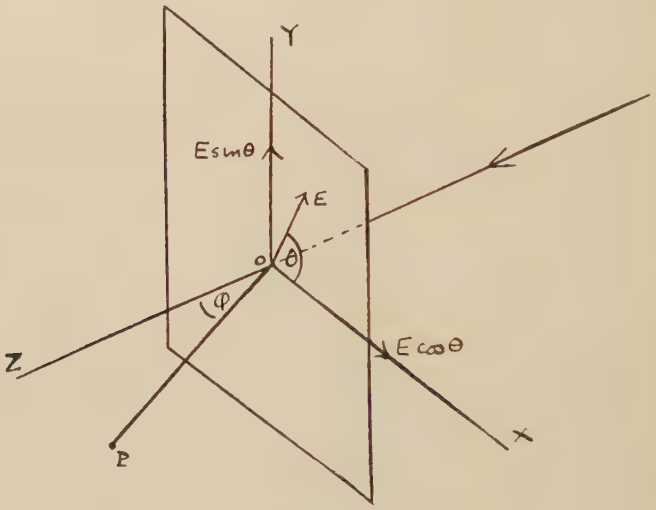


Fig. 1.

If $I_{\frac{\pi}{2}}$ is the intensity when $\phi = \frac{\pi}{2}$, then for the distribution of the secondary radiation we have the relation

$$I_\phi = I_{\frac{\pi}{2}}(1 + \cos^2\phi).$$

This is a symmetrical curve about the plane of the radiator showing a maximum value which is twice the minimum value. The ratio of the maximum to the minimum value has been experimentally determined by Barkla* and was found to agree very closely with theory.

Apparatus.

The X-ray bulb was placed horizontally inside a lead box. The beam was limited to a narrow pencil by lead stops placed inside a slightly conical lead tube L (Fig. 2). The lead tube

* Barkla, *Phil. Mag.* February, 1908.

extended to about half the distance between the radiator and the lead box, in order to reduce the air effect as much as possible.

The beam fell normally on a filter paper radiator R, which was much larger than the cross section of the beam at that point. It was suspended from a fixed support over a horizontal circular scale which was glued on top of a brass pivot O. A small needle was attached to the radiator which enabled the radiator to be replaced in exactly the same position each time it was removed.

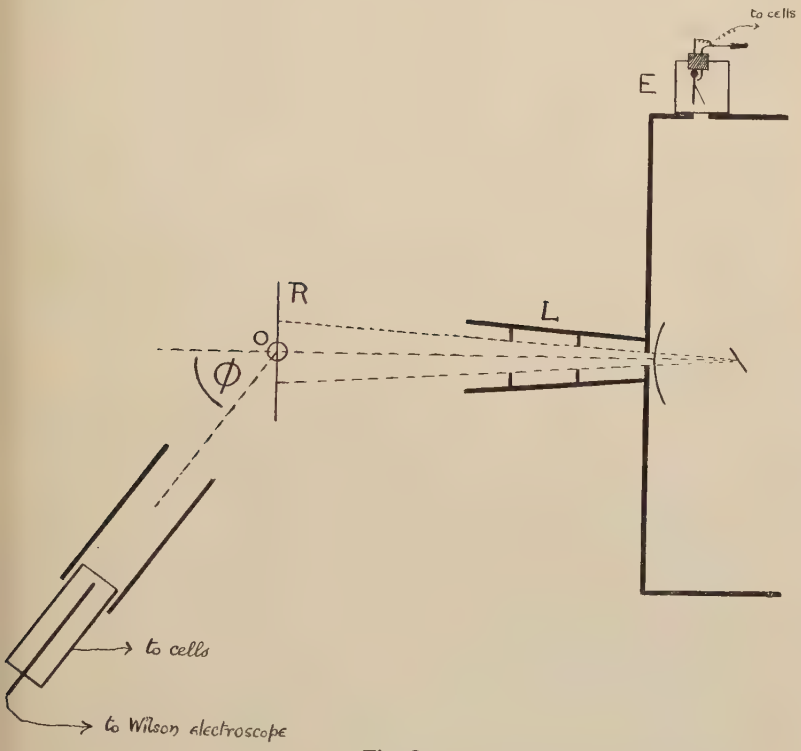


Fig. 2.

The ionization chamber, which was of the ordinary type with a central rod electrode, was mounted on a small platform at the end of a wooden arm which revolved about O. The central electrode was connected to an earthing key and a Wilson tilted electroscope, which were all carried with the ionization chamber on the small platform. The platform itself was supported by wheels which ran smoothly over a plate of glass, so that the leaf of the electroscope was not disturbed when the arm was moved from one position to the other. The glass plate was carefully

levelled so that the sensitiveness of the electroscope was practically unaffected by the position of the arm.

A lead cylinder lined with cardboard was placed, as shown, in front of the ionization chamber so as to receive the secondary beam from the radiator and cut down the air effect as much as possible. The distance from the radiator to the chamber was about 50 cm. and the width of the aperture of the chamber about 7 cm.; the aperture was covered up with a thin sheet of parchment. The distance from the bulb to the radiator was about a metre. The primary beam was standardised by an ordinary electroscope E placed so as to receive a portion of the primary beam.

For each position of the arm the following method of taking readings was adopted. The standardising electroscope was charged up to a definite potential (250 volts). The radiator was initially removed and the ionization produced in the chamber due to the secondary rays from the air was measured, whilst a fixed deflection was observed on the standardising electroscope. The rise of potential of the leaf in the Wilson electroscope was directly measured by means of a potential divider which was permanently connected to the needle of the earthing key.

The same procedure was repeated when the radiator was in position and again when it was removed. The mean of the air effect before and after the radiator was put in position was taken to be the true air effect. This effect was small in comparison with that of the radiator for medium and soft rays, but a little bigger for the hardest rays. The difference between the rise of potential of the leaf when the radiator was in position and when it was removed gave the actual ionization produced by the radiator alone.

The radiator consisted of sheets of thin filter paper which absorbed only a very small fraction of the incident beam. It was assumed for the radiators used, that the absorption of the hard and medium rays was negligible. The absorption for the softer rays, however, was allowed for as follows*.

If $I_{\phi r}$ and $I_{\phi t}$ be, respectively, the true intensities of the returned and transmitted secondary beams in a direction making an angle ϕ with the primary; I_{Or} and I_{Ot} the observed intensities, then we have

$$I_{\phi r} = \frac{d\lambda\,(\sec\phi + 1)}{1 - e^{-\lambda d\,(\sec\phi + 1)}} \cdot I_{Or},$$

$$I_{\phi t} = \frac{d\lambda\,(\sec\phi - 1)}{e^{-\lambda d \sec\phi}\left[e^{-\lambda d(1-\sec\phi)} - 1\right]} \cdot I_{Ot},$$

where d is the thickness of the radiator.

* *Vide* Crowther, *loc. cit.*

In deducing these formulae it was assumed that the absorbability of the secondary rays is the same as that of the primary rays. The value of $\frac{\lambda}{\rho}$ for the soft rays used was 1·5 for the filter paper radiator.

The results obtained after making the necessary corrections for absorption are given in Table I.

TABLE I.

Angle of arm with primary [ϕ]	Calculated values of $I_\phi/I_{\pi/2}$ [$=1+\cos^2\phi$]	Observed values of $I_\phi/I_{\pi/2}$		
		(*a*) Equivalent spark gap =7 cm.	(*b*) Equivalent spark gap =4·5 cm.	(*c*) Equivalent spark gap =2·5 cm.
150°	1·75	1·82	1·80	1·83
140°	1·59	1·59	1·59	1·59
130°	1·41	1·36	1·38	1·42
120°	1·25	1·11	1·13	1·10
60°	1·25	1·21	1·35	—
50°	1·41	1·38	1·69	1·72
40°	1·59	1·59	2·09	2·30
30°	1·75	1·76	2·73	3·11

Column (*a*) was obtained when radiator consisted of 12 sheets, and columns (*b*) and (*c*) with 24 sheets.

The distribution on the incident side of the radiator in each case agrees closely with the theoretical distribution given by the relation $I_\phi = I_{\frac{\pi}{2}}(1+\cos^2\phi)$. In the case of the hardest rays, the same theoretical distribution is also obtained on the emergent side for the positions examined. A dissymmetry, however, appears when the rays become softer, and this increases with the softness of the rays. It should be noticed that this dissymmetry is shown for all angles on the emergent side of the radiator.

The results are represented graphically in Fig. 3.

Experiments were made with radiators of different thicknesses, keeping the equivalent spark gap constant. In these cases only the readings at 30° with the primary on each side of the radiator were taken; these are given in Table II.

Hence the dissymmetry varies slightly with the thickness of the radiator—the relative intensity on the emergent side

increasing with the thickness. If, however, we continue to increase the thickness of the radiator beyond a certain limit the dissymmetry becomes less pronounced.

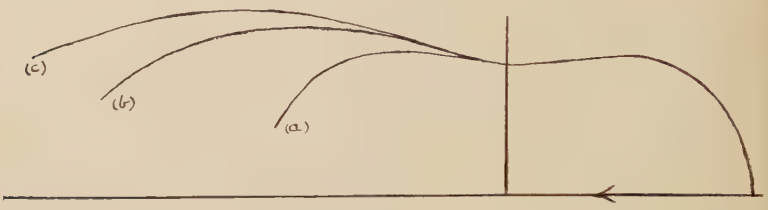


Fig. 3.

A possible explanation of the foregoing results is that the softer rays in the primary beam are irregularly refracted and become diffused. This effect superposed on the true scattered secondary rays would give an intensity which is greater on the emergent than on the incident side of the radiator for corresponding angles with the primary.

TABLE II.

Equivalent spark gap = 4·5 cm.		Equivalent spark gap = 2·5 cm.	
Thickness of radiator in sheets of filter paper	$\frac{I_t}{I_r}$	Thickness of radiator in sheets of filter paper	$\frac{I_t}{I_r}$
24	1·5	12	1·44
48	1·75	24	1·74

Experiments are in progress in which homogeneous rays are used for the primary instead of a beam direct from the X-ray bulb.

I am greatly indebted to Professor Sir J. J. Thomson for the encouragement he has given me and the keen interest he has taken in the work.

On the Velocities of the Electrons produced by Ultra-Violet Light. By A. Ll. HUGHES, M.Sc., B.A., Research Scholar of Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 27 March 1911.]

An accurate knowledge of the relations between the velocities of the electrons emitted from metals and the nature of the light and of the metal is essential for testing the truth of the different theories of the photo-electric effect. The velocities determined by experiment can only be employed with safety in the theoretical discussion of the photo-electric effect when we are satisfied that they are the actual velocities of emission from the molecules. The velocities of the electrons emitted by metals have been measured by Lenard*, Ladenburg† and Millikan and Winchester‡. The results obtained show considerable discrepancies, far larger than any possible error of experiment. The most probable explanation is that there is some kind of a film, probably of gas, present on the surface of metals which retards the electrons. It is hardly likely that the various methods of polishing the surfaces would leave the film in exactly the same condition. The velocities (expressed in volts) obtained by Ladenburg were 1·12 volts for Zn, 1·69 volts for Cu and 1·86 volts for Pt, using light of wave length λ2010.

v. Baeyer and Gehrts§ tried the effect of passing a discharge through the apparatus while it was being exhausted and found that, after this treatment, the maximum velocity was 6·3 volts for all the metals tested (Al, Cu, and Au). The shortest wave length emitted by the mercury lamp was taken to be λ2000. They found that the energy of the electron was given by the formula,

$$eV = hn,$$

where

$$e = 4{\cdot}69 \times 10^{-10} \text{ E.S.U.},$$

$$h = 6{\cdot}55 \times 10^{-27} \text{ erg. sec. (Planck's unit)},$$

$$n = \text{frequency}.$$

According to this formula, V (the potential required to bring the electron to rest) is 6·3 volts for light of wave length λ2000. They considered that this agreement between theory and experiment

* *Ann. d. Phys.* VIII. 1902, p. 152.
† *Verh. d. D. Phys. Gesell.* 1907, p. 166.
‡ *Phil. Mag.* XIV. 1907, p. 188.
§ *Verh. d. D. Phys. Gesell.* 1910, p. 870.

indicated that the surface film had been removed completely. On allowing the metal to stand in a "charcoal liquid air" vacuum, they found that the velocity gradually diminished and suggest that this is due to the formation of a surface film, probably of H_2 diffusing from the interior of the metal.

With a view to finding the true velocity of emission from the molecules, I have made experiments using surfaces which have been subjected to special treatment. The variations in the velocities after different kinds of treatment may be considered to be evidence of changes in the supposed surface film. The experiments tried include the effect of using the metal as anode, as cathode, of allowing the metal to stand in different gases and of preparing the metal surface by distillation *in vacuo*, wherever practicable. The source of light was a mercury arc in fused quartz. The limit of transparency of this may be taken to be about $\lambda 2000$.

Nickel.

The apparatus (similar to that used by v. Baeyer and Gehrts) for measuring the velocities of the electrons is shown in Fig. 1.

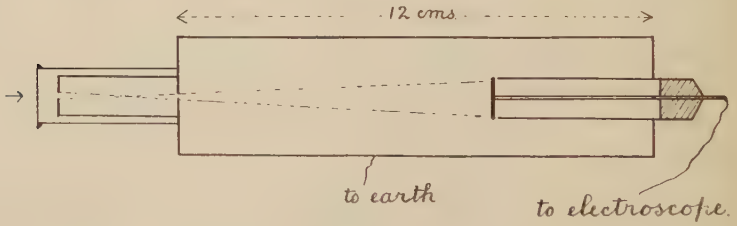


Fig. 1.

The case is earthed and the positive potential to which the plate rises is observed. All velocity measurements were made in a liquid air vacuum. The velocity obtained for each of two polished discs of Ni, without any special treatment, was 2·08 volts.

On using the Ni as cathode, it was found that the velocity rose considerably, usually to about 5 or 6 volts. Attempts were made to find the conditions under which the greatest increase was obtained. About sixty tests were made; the Ni was run as cathode for periods ranging from 5 to 60 mins., the pressure and nature of the gas used in the discharge were varied, and also the intensity of the discharge, but it could not be shown that any one of these factors had an appreciable influence upon the resulting velocities. Only five velocities higher than 6 volts were obtained, viz. 6·04, 6·60, 6·38, 6·40 and 6·74 volts. It was found that these

high velocities did not remain constant; there was a gradual decrease with the time. Three examples are given in the table.

Interval between readings	Velocity	Interval between readings	Velocity	Interval between readings	Velocity
35 mins.	6·38 volts	55 mins.	5·06 volts	25 mins.	6·04 volts
15 hours	6·24 ,,	21 ,,	4·64 ,,	125 ,,	5·98 ,,
48 ,,	4·32 ,,	28 ,,	4·61 ,,		5·94 ,,
	3·92 ,,	135 ,,	4·50 ,,		
		14 hours	4·22 ,,		
			3·94 ,,		

Running the Ni as anode, after a high velocity had been obtained, appeared to have but little effect on the velocity.

Some interesting results were obtained on admitting different gases into the apparatus. The Ni was used as cathode in order to get an increased velocity, this was measured and then the gas was admitted at a pressure of 10 cms. for 10 mins. The results for O_2, CO and H_2 are given in the following table.

Velocity after use as cathode	Velocity after contact with gas	Reduction in velocity
O_2 5·06 volts	... ... 3·54 volts	1·52 volts
	13 hours later 3·74 ,,	
O_2 6·74 ,,	... ... 5·30 ,,	1·44 ,,
	100 mins. later 5·52 ,,	
	90 mins. later 5·40 ,,	
CO 4·54 ,,	... ... 3·84 ,,	·70 ,,
	30 mins. later 3·94 ,,	
H_2 4·26 ,,	... ... 4·18 ,,	·06 ,,
	40 mins. later 4·12 ,,	
H_2 5·90 ,,	... ... 5·52 ,,	·38 ,,
	40 mins. later 5·63 ,,	at 10 cms. for 40 mins.

It will be noticed that O_2 produces the greatest reduction and H_2 the least. A peculiar feature is that after the gas has produced a decrease in the velocity, a small but decided increase follows. It might be urged that the first reading was taken before the high vacuum was fully established. To test this, the velocity was measured in a liquid air vacuum (< ·0005 mm.) and then at a pressure of ·019 mm. air (free path of an electron 2·5 cms.) and the difference was not greater than ·02 volt. The pressure was always taken down to about ·03 mm. by a Toepler pump before communication with the charcoal tube was made. As readings were not taken until 10 mins. had elapsed, there was ample time for a sufficient exhaustion to take place.

Copper.

The emission velocities obtained for three different discs of polished Cu before using them as electrodes were 1·46, 1·32 and 1·66 volts.

The effect of running the Cu as cathode was almost always to increase the velocity. As in the case of the Ni, the amount by which the velocity altered varied to a great extent in different experiments and could not be connected with any of the conditions governing the discharge. The greatest emission velocity obtained for Cu was 4·44 volts. On allowing the Cu to stand in the vacuum a gradual decrease in the velocity was observed.

The effect of using the Cu as anode was to reduce the velocity usually below the normal value for polished Cu. The following table gives the results of using the Cu as an anode for 5 mins.

Velocity before use as anode	Velocity after anode
4·44 volts	... ... 1·72 volts 10 mins. later 1·96 „
2·38 „	... ... ·82 „ 2 hours later 1·02 „
1·74 „	... ... 1·08 „
2·42 „	... ... ·92 „ 20 mins. later 1·04 „

The gas used while the discharge was taking place was O_2 in the first three experiments and H_2 in the last experiment.

Experiments were made on contact with O_2 and H_2 as in the case of the Ni. There appeared to be no definite diminution in the velocity after contact with H_2, while a decided reduction was observed after contact with O_2, though it was not so marked as in the case of the Ni. This was to be expected, since the velocities obtained after use as cathode were usually about 2 volts less with the Cu than with the Ni.

Zinc.

It has been tacitly assumed that the velocities obtained from ordinary polished metals are less than the true velocities of emission from the molecules on account of a retarding surface layer. Some doubts may be expressed as to the view that the effect of using a metal as an electrode is simply to remove, partially or completely, the surface film, and it is therefore desirable to try some other method of obtaining a surface free from this film.

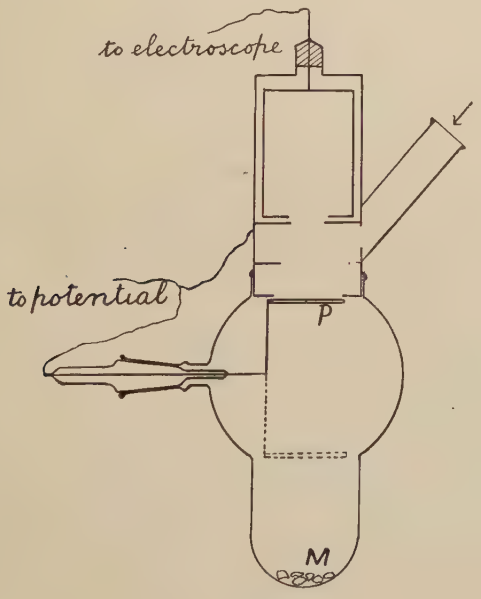


Fig. 2.

It was found that surfaces of Zn and Cu could be prepared by distillation *in vacuo*. A new form of apparatus had to be designed for experiments with distilled metals (Fig. 2). The maximum velocity of the electrons from the plate P was given by the smallest positive potential necessary to stop the electrons from

entering the Faraday cylinder. The metal to be distilled was placed at the bottom of the glass tube at *M*. When the metal was first heated some gas was evolved and for this reason the plate *P* was not turned downwards until the evolution of gas had practically ceased. The distillation always took place in a liquid air vacuum.

Two different samples of Zn were used for distillation. The velocities of emission from the two distilled surfaces were 2·20 volts and 2·28 volts. The velocities changed but very little with the time; after standing for 17 hours in a high vacuum the velocity diminished from 2·20 to 2·15 volts. On admitting H_2 at 10 cms. for 10 mins. to the apparatus no change was observed. On admitting O_2 at 10 cms. for 10 mins. the velocity changed from 2·24 volts to 1·83 volts. After an interval of 30 mins. it rose to 1·94 volts at which it remained. After two days' exposure to air at atmospheric pressure the velocity fell to 1·66 volts, which is still appreciably higher than Ladenburg's value for polished Zn, viz. 1·12 volts.

An electrode was introduced at *M* and a discharge could be passed between it and the plate *P* in the dotted position. After running the distilled Zn surface as a cathode, the velocity increased considerably, the highest value obtained being 5·76 volts. The velocities so obtained decreased very rapidly with the time, after 4 mins. the velocity was 5·4 volts, 7 mins. later it was 5·0 volts. This rapid decrease was always noticed.

As before, the presence of H_2 had no appreciable effect on the velocity, while O_2 at 10 cms. for 10 mins. reduced the velocity from 3·86 to 2·80 after which it rose to 2·98 volts.

Cadmium.

Two specimens of Cd were used for distillation. The first was ordinary commercial Cd and the second was Cd obtained by precipitation by Zn from a gas-free solution of cadmium iodide.

The velocities obtained after three different distillations were 2·01, 1·93 and 2·05 volts, the latter being for Cd from the solution. As with the distilled Zn, there was but little change in the velocity with the time. The reduction of the velocity by O_2 was of the same order as in the case of the Zn.

Mercury.

For experiments on mercury distilled *in vacuo*, the glass portion of the apparatus in Fig. 2 was removed and a more suitable arrangement substituted. Two distillations were made and the maximum velocities were found to be 2·12 and 2·22 volts.

Discussion of Results.

It is somewhat difficult to find a reliable criterion to decide whether a surface is free from any retarding film. On general considerations, one might expect that a surface prepared by distillation *in vacuo* would more likely be free from a surface film than a surface which had been treated by a discharge. The latter process might conceivably involve the deposition of a film charged relatively to the surface which would (positive layer outside) accelerate the electrons emitted from the metal. The distillation process is entirely free from an objection of this kind and it is more satisfactory in one respect, viz. that it can be carried out in a better vacuum. It seems hardly likely that the surface film can be carried over, even partially, in the process of distillation, and finally appear on the surface of the distilled metal. One fact favourable to the distillation method is that the increased velocities obtained are much more constant and remain steadier than the values obtained after a discharge. Assuming that the increased velocities after a discharge are produced by an accelerating film one would expect this to break up more rapidly than a film would form *in vacuo* on a surface initially free.

On comparing experiment with one form of the theory, it appears that the evidence is in favour of regarding a film as being removed when a discharge has resulted in a velocity of 6·3 volts. It was mentioned above that v. Baeyer and Gehrts obtained velocities after a discharge which were in agreement with Planck's theory. It must be remembered, however, that there was an assumption that the whole of the energy $h\nu$ in the light unit is given to the expelled electron. On consideration of the great variations in the velocities which I obtained after using the nickel as an electrode, doubts may be expressed as to whether still higher velocities might not be obtained by this method, apart from theoretical predictions. Using the same source of light as v. Baeyer and Gehrts, I obtained on four occasions emission velocities greater than 6·3 volts, the highest being 6·74 volts. If Planck's theory is applicable in the form given above, this would require the fused quartz of my mercury lamp to transmit as far as $\lambda 1860$.

Joffé* examined Ladenburg's results and found, on plotting the energy of the electrons against the frequency, that a straight line was obtained which, however, did not pass through the origin. From the point where the line cuts the axis of energy it may be concluded that there was a surface double layer, the difference of potential being about 1 volt. Now the velocity obtained by

* *Ann. d. Phys.* xxiv. 1907, p. 939.

Ladenburg for Zn was 1·12 volts. If the retarding layer were absent, the true velocity of emission would be about 2·1 volts, which is approximately the same as that which I obtained for distilled zinc. The gradient of the line connecting energy and frequency implies that only a part of the energy in the light unit is given to the electron. To settle the question it is desirable to measure the velocities corresponding to different wave lengths using distilled metals as the illuminated surfaces. If the line obtained passes through the origin, it will be strong evidence that the retarding layer is absent.

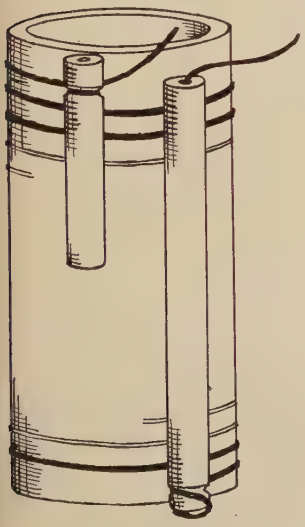
The gradual decrease in the velocity of emission after a big value had been obtained was suggested by v. Baeyer and Gehrts to be due to some gas, probably hydrogen, diffusing out of the metal and slowly forming a surface film. The experiments recorded above do not support this view, as the emission velocities were least affected by hydrogen. Oxygen was found to produce a marked decrease, which, however, was followed by a slight increase. This suggests that the film formed in this way is not so tenacious as the film on ordinary surfaces.

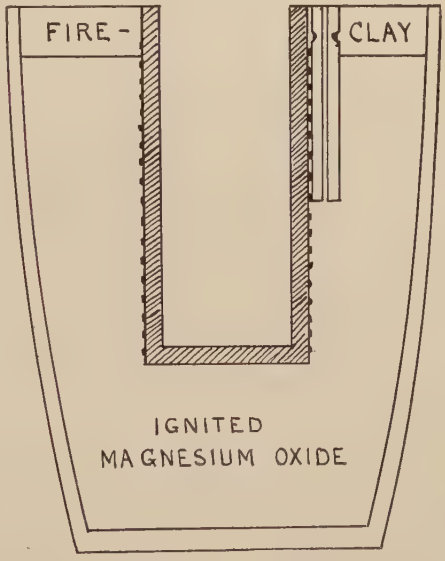
I wish to thank Professor Sir J. J. Thomson for his interest and suggestions during the course of the work.

A simple form of Electrical Resistance Furnace. By F. E. E. Lamplough, M.A., Trinity College.

[*Read* 13 March 1911.]

In order to measure the freezing points of certain salts attempts were made to construct an electrical resistance furnace. In such a furnace there are no reducing gases nor hot products of combustion, and the labour and noise of blowing and consequent attention are obviated, whilst the rate of cooling is under complete control, making the furnace most useful for determining freezing points and arrests and for annealing, etc.





Around a porcelain crucible of about 5 cms. diameter and 11 cms. length a coil of platinum wire or ribbon was wound. For one furnace about 3 metres of platinum wire ·33 mm. diameter was used, and this was rolled out slightly to make a very narrow ribbon, the leads being three strands of the same wire.

The separate turns were about 4 mm. apart, and were held in position by a paste of fireclay, magnesia and water applied to the crucible so as just to cover the wire, the ends being secured as shown in the diagram by winding round two pieces of clay pipe-stem attached by fireclay to the crucible. The lead from the lower end of the coil was brought up through one of these stems. When dry and hard the whole was placed in a large Battersea crucible and tightly packed in with magnesia which had been previously ignited at a high temperature, the magnesia being held in by a covering of fireclay. Such a furnace gives a temperature of 1200° C., and to maintain at this temperature an expenditure of about 450 watts is required, and much less at lower temperatures.

On an attempt to detect Diffusion in a Pencil of Röntgen Rays.
By J. A. Crowther, M.A., St John's College.

[*Read* 13 March 1911.]

The experiments described in the following paper were undertaken in order to discover whether a narrow pencil of Röntgen rays suffers any direct diffusion or irregular refraction in passing through matter. In a previous paper* I have investigated the

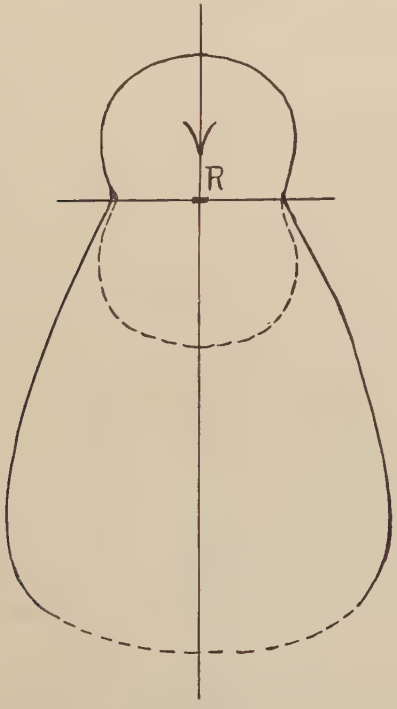


Fig. 1.

distribution of the scattered Röntgen radiation round the radiator and have shown that there is a lack of symmetry in the scattered radiation which would not have been expected from the simple theory of the phenomenon. The results obtained are shown in

* *Camb. Phil. Soc. Proc.*, Nov. 1910.

Fig. 1. Here the radiator is supposed to be at R, and the intensity of the scattered radiation in any direction is given by the length of the vector drawn from R in that direction. The primary beam is in the direction of the arrow. The dotted curve gives the theoretical distribution to be expected on the simple theory; the full curve represents the results actually obtained with a radiator of aluminium, ·308 mm. thick. It will be seen that the experimental curve for the forward loop lies entirely outside the theoretical curve. The forward radiation is at every angle greater than the returned.

Barkla*, who has more recently published some measurements of the same phenomenon, only obtains this dissymmetry in directions very close to the primary beam; but Owen†, who has repeated my experiments in the Cavendish Laboratory, has obtained results which for soft radiations confirm those which I obtained.

The form of the experimental curve suggests that the radiation measured is of two kinds: (1) the true scattered radiation distributed according to the theoretical formula, (2) a superposed radiation from some other source, the intensity of which diminishes continually as we get further away from the forward direction of the primary beam. If two sources of radiation exist, the type of rays they cause to be emitted must be the same, as there is no appreciable difference in the absorbability of the forward and backward radiation.

It has been suggested that the cause of the dissymmetry might be found in a diffusion or irregular refraction of the primary rays by the substance of the radiator. Let us suppose that the primary Röntgen pulse in passing through the field of an atom is deflected through some small angle α. The direction of this deflection will be perfectly arbitrary, and, the atoms being sufficiently numerous, we can compound these arbitrary deflections by means of the theorem due to Lord Rayleigh on the composition of random displacements. It can be shown that the probability of a displacement between the angles θ and $\theta + d\theta$ is

$$\frac{1}{n\alpha^2}\, e^{-\frac{\theta^2}{n\alpha^2}}\, \theta \,.\, d\theta,$$

where n is the number of atoms traversed by a pulse in passing through the radiator; and the probability of a deflection greater than θ is given by $e^{-\frac{\theta^2}{n\alpha^2}}$.

If we now assume that the difference between the experimental and the theoretical curves for the scattered radiation is due to an

* *Phil. Mag.*, Feb. 1911.
† *Camb. Phil. Soc. Proc.*, 1911.

effect of this nature, we can from our curves obtain a value for the latter quantity, and thus calculate the value which the constant $n\alpha^2$ must have in order to account for the effects observed. From the value of the constant so obtained we can then calculate what value the radiation should have at any angle with the primary beam due to this diffusion. This intensity will increase as we approach the primary beam. Experiments made close to the primary beam should therefore enable us to decide whether any appreciable diffusion exists, and whether it is sufficiently great to explain the dissymmetrical distribution with which we have been dealing.

TABLE I.

θ	I	$\sin\theta$	$I\sin\theta$
*1°·5	11·4	·026	0·30
*4°	11·4	·069	0·69
25°	10·5	·423	4·45
30°	9·98	·500	4·94
40°	4·93	·643	3·17
60°	3·34	·866	2·90
70°	2·88	·940	2·79
110°	2·40	·940	2·26
130°	2·92	·766	2·24
145°	3·30	·674	1·90

* These figures are deduced from the measurements in the present paper.

Table I, which is taken from a previous paper, contains the experimental numbers for an aluminium radiator 0·0308 cm. thick. The first column gives the angle θ between the primary beam and the mean direction in which the intensity of radiation is measured; the second column gives the measured intensity I of the radiation through a given small area in this direction, corrected for the absorption of the primary and secondary radiation. The whole intensity of radiation in the cone between the angles θ and $\theta + d\theta$ is proportional to $I\sin\theta$. The values for this quantity are given in the last column of the table. Plotting these values against the corresponding values of θ, we get a figure (Fig. 2), the area of which measures the whole scattered radiation round the radiator.

On the assumptions made, some of the diffused beam would be present even in the radiation returned from the radiator. Its amount would be very small, and in order to obtain a minimum value for the amount of diffusion necessary, we will neglect it, and

regard the returned radiation as being purely scattered. The scattered radiation in the forward half of the figure will therefore be represented by the lower curve which is the mirror image of the curve for the return radiation, in the plane $\theta = 90°$. The whole area of the curve gives the whole intensity of scattered radiation as measured in the previous experiments. The area included between the two curves and the ordinate $\theta = 30°$ gives the intensity of the radiation beyond 30° which we propose for the present to ascribe to the diffusion of the primary beam by molecular refraction. On these assumptions its value is $Ie^{-\frac{\theta^2}{n\alpha^2}}$, where $\theta = 30°$.

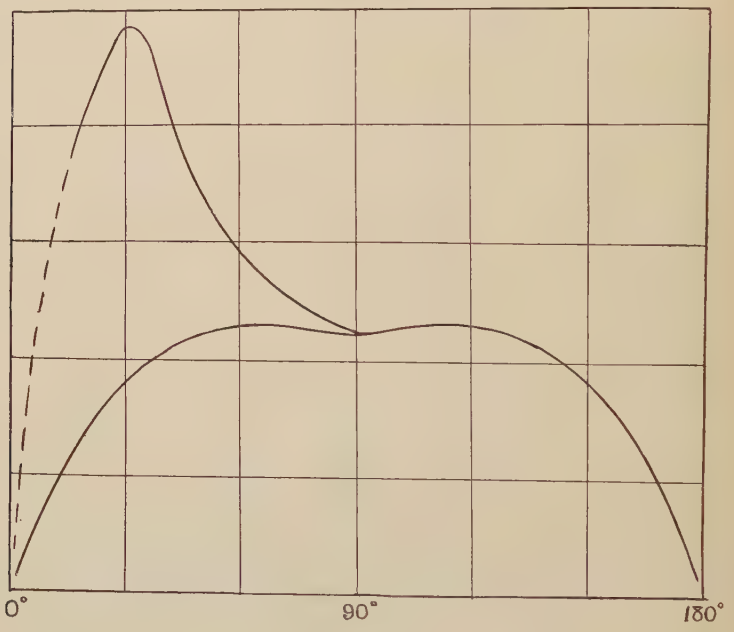


Fig. 2.

Plotting the curves on squared paper and measuring up the areas we find that the outstanding radiation beyond the angle of 30° is 0·095 of the whole area of the curve. The radiation to be ascribed to diffusion is therefore 0·095 of the total radiation measured. It has been shown in a previous paper* that the intensity dS of the scattered radiation from an element of mass per unit area dm is given by

$$dS = k \,.\, I \,.\, dm,$$

* J. A. Crowther, *Proc. Roy. Soc.*, A, lxxxv. p. 30, 1911.

where I is a constant whose value has been found to be about 1·1. The figures given in the table have been already corrected for absorption; we may write therefore

$$S = k \,.\, I_0 \,.\, m.$$

The density of aluminium being 2·7, and the thickness of our radiator 0·0308 cm.; m is equal to 0·083 gm. per sq. cm. We have therefore

$$S = \cdot 083 \times 1 \cdot 1 \times I_0$$
$$= \cdot 090 \; I_0.$$

Hence the residual radiation which is equal to ·095 S equals $\cdot 095 \times \cdot 090 \,.\, I_0$, that is ·0085 I_0. Equating this to $I_0 e^{-\frac{\theta^2}{n\alpha^2}}$, where θ is now 30° (or ·53 radian), we have

$$I_0 e^{-\frac{\theta^2}{n\alpha^2}} = \cdot 0085 \; I_0,$$
$$e^{-\frac{(\cdot 53)^2}{n\alpha^2}} = \cdot 0085,$$
$$n\alpha^2 = \underline{\cdot 057}.$$

With a constant so small as this, it was evident that a very small diffusion of the primary beam would suffice to account for the observed effects, and that special apparatus would have to be devised to detect it. It was calculated that an intensity of between 1°/₀ and 2°/₀ of the primary beam was all that could be expected between angles of 1° and 2° with the primary beam.

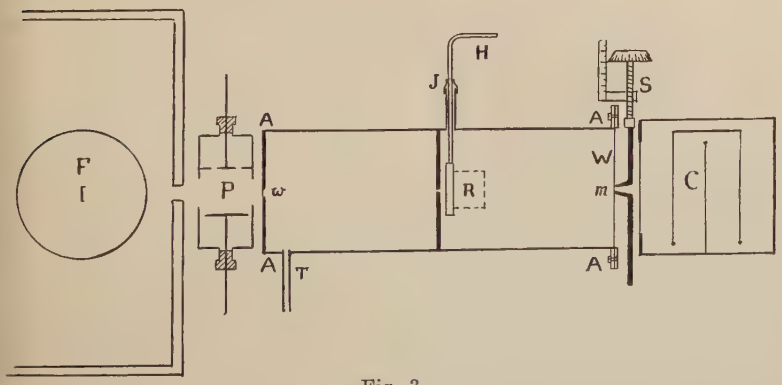


Fig. 3.

Before proceeding further with the calculations it will be necessary to describe briefly the apparatus employed. It is shown diagrammatically in Fig. 3. In the earlier experiments on scattering, a certain amount of trouble had been experienced, especially as the direction of the primary beam was approached, from the

scattered radiation from the air. It was decided therefore to have the path of the primary beam from the focus tube to the ionization chamber in a vacuum. $AAAA$ is a rectangular brass box $30 \times 10 \times 4$ cms., one end of which is closed by an aluminium window W. At the other end of the box a narrow slit w, also closed with thin aluminium foil, serves to admit the primary rays from the focus tube F. At the centre of the box a second slit a, 1·2 cms. long by 0·20 cm. wide and placed parallel to the slit w, serves to limit the primary rays to a narrow rectangular beam. A lead shutter with a narrow slit m, 3·45 cms. long by 0·23 cm. wide, can be moved across the window W by means of a screw S with a graduated head; its direction of motion being at right angles to the primary beam.

The intensity of the radiation emerging through the slit m is measured by means of a Wilson electroscope connected to the ionization chamber C. A second chamber P serves to standardise the primary rays.

The radiator R is mounted on a rod working in an air-tight joint J, and can be inserted or removed from the path of the rays by turning the handle H. The whole box can be evacuated through a side tube T.

Measurements were made for various positions of the slit m as it was moved gradually across the primary beam. When any portions of the primary beam itself were included in the area covered by the slit it was necessary to insert additional capacities into the electroscope system of from ·001 to ·005 microfarads. The capacity of the electroscope system itself was compared directly with these capacities by the method recently described by N. R. Campbell in the *Philosophical Magazine*. Knowing the ratios of the various capacities, the ratios of the ionization currents, and therefore of the intensities of the radiations, could be immediately obtained. The results obtained for different positions of the slit are given in Table II.

The first column of this table gives the position of the slit m in terms of the scale reading of the screw S. The second and third columns give the intensity of radiation passing through the slit when in the given position without and with the radiator. These values have been corrected for the variations in the intensity of the primary beam, as given by the ionization chamber P. In the case of the readings outside the range of the primary beam, correction has also been made for the spontaneous ionization in the chamber C.

Taking first the readings made without the radiator, in order to get some idea of the nature of the primary beam, we find that the intensity is at first practically zero. There is always a small outstanding effect after correcting for the spontaneous ionization,

but it is very small and is probably due to some scattered radiation from the edges of the slits. If now we move the slit in towards the primary beam we find that the intensity remains constant at this small value until we reach a position between the scale readings 6·90 and 6·85. Here the intensity suddenly becomes appreciable and increases very rapidly as we move our slit further and further across the primary beam. A maximum is reached at about 6·60, and the intensity then falls off again, regaining its initial small value between the positions 6·26 and 6·20.

TABLE II.

Position of Shutter	Intensity of Radiation	
	Without Radiator	With Radiator
7·50	·00004	·00014
6·90	·00004	·00014
6·85	·00180	·00129
6·80	·050	·031
6·70	·163	·114
6·60	·445	·363
6·50	·396	·282
6·40	·160	·100
6·26	·00225	·00176
6·20	·00004	·00014
6·10	·00004	·00014

Regarding the source of the primary rays as a point situated on the anti-cathode, the cross section of the primary beam in the plane of the shutter will be a rectangle 2·8 mm. in width. Our measurements show that the centre of this rectangle must occupy the position given by the reading 6·56 on the scale of the screw. The rapid falling off of this intensity as we pass away from this position shows that there is very little of the primary radiation outside the limits of the geometrical image. Assuming that the primary rays are distributed uniformly over the area of cross section (which our measurements show to be at any rate approximately the case), we can proceed to calculate the intensity to be expected across the slit m in any given position when the given radiator is placed in the path of the primary rays.

Let O (Fig. 4) be a point on the radiator in the path of the primary rays, and let i be the intensity of the primary radiation through a small area at O. The intensity of the diffuse radiation

from this small area included in the conical shell bounded by the angles θ and $\theta + d\theta$ is given by

$$i \frac{2}{n\alpha^2} \cdot e^{-\frac{\theta^2}{n\alpha^2}} \theta \cdot d\theta.$$

This can be written

$$i \cdot \frac{2}{n\alpha^2} e^{-\frac{\theta^2}{n\alpha^2}} \frac{\theta}{\sin\theta} \frac{d\omega}{2\pi},$$

where $d\omega$ is the solid angle in the conical shell.

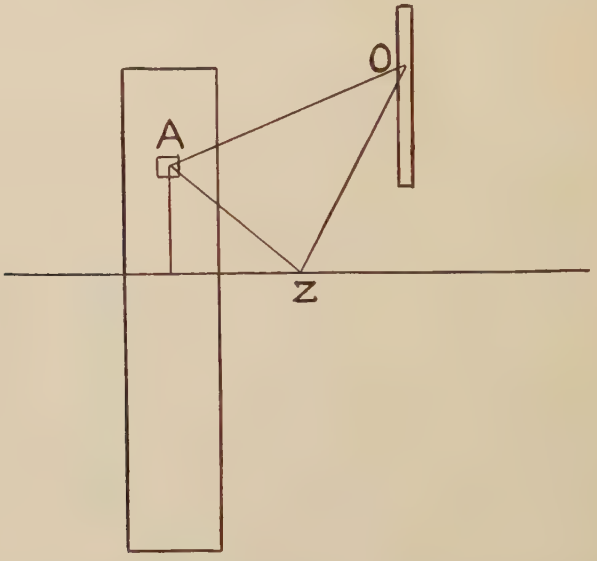


Fig. 4.

As we are dealing only with positions of the slit very close to the primary beam, θ is always small, and we can write $\theta/\sin\theta$ as unity. The intensity in the conical shell thus becomes

$$\frac{i}{\pi n\alpha^2} \cdot e^{-\frac{\theta^2}{n\alpha^2}} d\omega.$$

Let O be taken as the origin of co-ordinates, and the direction of the primary ray through O as the axis of Z. Consider a small area $dx \cdot dz$ of the slit m situated at a point A with co-ordinates x, y, z, where z will be the distance of the plane of the shutter from the radiator. Then for this area we have

$$d\omega = \frac{dx \cdot dy}{z^2} \cos\theta,$$

where θ is the angle ZOA, and $\cos\theta = \frac{z^2}{z^2 + x^2 + y^2}$.

But z is very large compared with the distance of the slit from the primary beam, and with the dimensions of the slit; we may therefore write $\cos\theta = 1$, without introducing an error of more than $2^{\circ}/_{\circ}$. Similarly we may put $\theta = \frac{\sqrt{x^2+y^2}}{z}$. The whole intensity of radiation through the slit m due to the diffuse radiation from the small area at O is therefore

$$I = \frac{i}{z^2\pi \,.\, n\alpha^2} \int_{a_1}^{a_2}\int_{b_1}^{b_2} e^{-\frac{x^2+y^2}{z^2\,.\,n\alpha^2}}\,.\,dx\,.\,dy,$$

where a_1, a_2, b_1, b_2 are the co-ordinates of the edges of the slit m. This integral may be written in the form

$$I = \frac{i}{z^2\pi \,.\, n\alpha^2}\cdot\int_{a_1}^{a_2} e^{-\frac{x^2}{z^2\,.\,n\alpha^2}}\,dx \times \int_{b_1}^{b_2} e^{-\frac{y^2}{z^2\,.\,n\alpha^2}}\,dy.$$

Putting $t = \frac{x}{z\sqrt{n\alpha^2}}$ and $t = \frac{y}{z\sqrt{n\alpha^2}}$ respectively in the two integrals, we have

$$I = \frac{i}{z^2\pi \,.\, n\alpha^2}\, z^2\,.\,n\alpha^2\,.\int_{\frac{a_1}{z\sqrt{n\alpha^2}}}^{\frac{a_2}{z\sqrt{n\alpha^2}}} e^{-t^2}\,dt \times \int_{\frac{b_1}{z\sqrt{n\alpha^2}}}^{\frac{b_2}{z\sqrt{n\alpha^2}}} e^{-t^2}dt\,;$$

or writing $K(x)$ for the value of the function

$$\frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt,$$

we have finally

$$I = \frac{i}{4}\left[K\left(\frac{a_2}{z\sqrt{n\alpha^2}}\right) - K\left(\frac{a_1}{z\sqrt{n\alpha^2}}\right)\right]\left[K\left(\frac{b_2}{z\sqrt{n\alpha^2}}\right) - K\left(\frac{b_1}{z\sqrt{n\alpha^2}}\right)\right].$$

The values of $K(x)$ can be ascertained directly from a table of probability integrals. Substituting the values for the constants a_1, a_2, b_1, b_2, and the calculated value of the constant $n\alpha^2$, we can at once find the intensity of radiation to be expected from any given point in the radiator.

The area of the radiator struck by the primary beam is not indefinitely small. Strictly, we should integrate again over the area of the radiator which is under the influence of the primary beam. This could easily be done by graphical methods. On substituting the constants, however, it is found that the value obtained does not vary very much over the very small area of the cross section of the primary beam. Thus taking $n\alpha^2 = \cdot 057$ as the value which this constant must have in order to account for the dissymmetry observed, and taking the slit in the position given by the scale reading 6·90 cm., we find that the intensity over the area of the slit m from an area situated at the very

centre of the cross section of the primary beam should be ·0201 I, where I is the intensity of the primary beam through that area. If the area had been taken on the edge of the primary beam nearest to the slit m, this intensity would have risen to ·0206 I; while for the further edge it would have fallen to ·0199 I. Similarly, proceeding up the cross section of the primary beam the intensity of the diffuse radiation only falls off from ·020 I to ·019 I. For our present purpose it will be quite sufficient to take a mean value. We thus find that in order to account for the dissymmetry actually observed in the scattered radiation, the intensity of the radiation over the area of the slit m in the position 6·90 cms. on the screw scale, or 0·34 cm. from the centre of the primary beam, should be ·020 I or just about one-fiftieth of the intensity of the primary beam.

We have not considered the effect of the absorption of the rays in the radiator on the measured intensity. Since the slit is so near the primary beam the path of the diffuse radiation and of the primary radiation in the radiator is practically the same. As the two radiations are identical in type the absorption must therefore be the same for both. We can therefore correct for this absorption by taking as the value of I the intensity of the primary radiation as measured through the radiator. As the slit m had a smaller width than the cross section of primary beam in the plane of the slit we must multiply the value observed by the ratio of the two, *i.e.* by 2·8/2·3, in order to obtain the total intensity of the primary beam.

Turning to the last column of Table II we find that the measured intensity of the primary rays after transmission through the radiator is ·363 in the units adopted for this experiment. The total intensity of the transmitted primary rays is therefore ·363 × 2·8/2·3 or ·44. The intensity of the radiation through the slit in the given position should therefore be ·44 × ·020, or ·0088 in the units of the experiment. Turning again to the last column of Table II we see that the intensity actually observed with the slit in this position (6·90 cms.) is only ·00014, or not more than 2°/₀ of the required intensity. It seems therefore that the dissymmetry of the scattered radiation cannot be ascribed to a diffusion of the primary by an irregular molecular refraction.

The test is even more severe than it appears, as in order to obtain as large an effect as possible, a much thicker radiator (0·63 gm. per sq. cm.) was employed in these diffusion experiments than was used in the previous experiments on the scattered radiation.

The present experiments enable us to complete our curve for the distribution of the scattered Röntgen radiation in the neighbourhood of the primary beam. The results have been included

in Table I. They show that the scattered radiation does not increase indefinitely as the primary beam is approached, but that the distribution curve forms a double loop as shown in Fig. 1.

Summary.

Experiments have been made on the scattered Röntgen radiation from a radiator in directions very close to the primary beam. It has been found that the distribution of the scattered radiation is not consistent with the supposition that the dissymmetry observed in the distribution is due to an irregular refraction of the primary beam by the atoms of the radiator.

Further Experiments on Scattered Röntgen Radiation. By J. A. Crowther, M.A., St John's College.

[*Received* 4 April 1911.]

The following note gives a brief summary of the further experiments which have been made to investigate the dissymmetry observed in the distribution of the scattered radiation from a radiator under the action of a beam of primary Röntgen rays.

(1) Attempts have been made to influence the distribution of the scattered radiation by a strong magnetic field. The radiator was placed between the poles of a strong electro-magnet and measurements were made of the scattered radiation in various directions with and without the magnetic field. Within the limits of experimental error no difference could be detected between the two sets of readings. The maximum field applied was 2500 gauss.

(2) Similar experiments were tried with electric fields. A paraffin radiator coated on each side with aluminium leaf to make electrical contact was used, but although fields of as much as 22,500 volts per cm. were applied no difference could be detected in the scattered radiation with and without the field.

It is possible that under more severe conditions some effect might be observed. The experiments are being continued.

The adaptation of Ticks to the habits of their Host. By Professor NUTTALL.

[*Read* 20 February 1911.]

A survey of our present knowledge of the structure and biology of the Ixodoidea appears to warrant certain conclusions. These must, however, be regarded in part as provisional and subject to revision when our knowledge of the various species of ticks has become more extended. The views here expressed may prove of practical use in the study of the *Ixodidae*.

The *Argasidae* represent the relatively primitive type of ticks because they are less constantly parasitic than are the *Ixodidae*. Their nymphs and adults are rapid feeders and chiefly infest the habitats or resting places of their hosts. In certain *Argasidae* (*O. moubata* and *O. savignyi*) the disadvantage of their possessing an "active" larval stage has resulted in the development of an "inactive" larva, *i.e.* the young nymph being the first to suck blood. In *O. megnini* we have a considerable adaptation brought about by the difficulty there must be in the tick entering the small aperture of the ear more than once. Owing to the *Argasidae* infesting the habitats of their hosts, their resistance to prolonged starvation and their rapid feeding habits, they do not need to bring forth a large progeny, because there is less loss of life, as compared to *Ixodidae*, in the various stages prior to their attaining maturity.

The *Ixodidae* are more highly specialised parasites than the preceding. The majority (Group Metastriata) are parasitic on hosts having no fixed habitat, and consequently all stages, as a rule, occur upon the host. In the genus *Ixodes* (Prostriata) we find an adaptation of certain species according to the habits of the hosts upon which they are parasitic. In the species which usually occur upon wandering hosts both sexes are found upon the host, whereas in other species which occur on hosts possessing more or less fixed habitats the males are rarely or never found upon the host. The males of species of *Ixodes*, both sexes of which occur upon the host, usually possess hypostomes with prominent teeth, the reverse being the case in forms wherein the males do not occur upon the host. Where species occur upon a wandering host it is essential, for their propagation in nature, that both sexes should be carried about upon the host.

It follows that the copulation of ticks upon the host is an indication of a higher degree of specialisation to a life of parasitism. When copulation does not take place on the host, we have merely the retention of a primitive character as found in *Argasidae*. It appears to me that many species of *Ixodes* are known to science only in their female and immature stages simply because the males have not as yet been sought for in the habitats of their hosts.

A great many males of Metastriata are known; this holds for *Haemaphysalis*, *Dermacentor*, *Rhipicephalus*, *Amblyomma* and *Aponomma*, to mention genera of *Ixodidae* that are rich in species. The males of *Boophilus*, *Hyalomma*, *Rhipicentor* and *Margaropus*, of which there are few species, are likewise known. In all of these genera the males are found together with the females upon the host. These genera are chiefly parasitic on animals with wandering habits, and the males of these genera do not exhibit hypostomes which are markedly dissimilar to those of the females as in the case of *Ixodes*.

Toleration to Nicotine. By W. E. Dixon, M.A., Downing College.

[*Read* 20 February 1911.]

One form of toleration to chemical substances is associated with their destruction and oxidation; the tolerance to alcohol and morphine are examples. In the case of nicotine it has been found that normal animal tissues have the power to destroy a small quantity of the alkaloid. The tissues of animals which have been rendered tolerant to nicotine destroy a considerably larger amount. There is evidence to show that the destruction of the nicotine is not due to a chemical combination with the tissues but that, on the contrary, it is brought about by ferment action.

The Action of Pituitary Extract and Adrenalin on Peripheral Arteries. By Dr Cow. (Communicated by Mr W. E. Dixon.)

[*Read* 20 February 1911.]

Employing the method of O. B. Meyer—adrenalin constricted the peripheral arteries with the exception of the intravisceral portion of the pulmonary, the coronary and cerebral arteries. The coronary and cerebral vessels were dilated and the intravisceral portion of the pulmonary was unaffected. Pituitrin produced dilatation of the splenic, hepatic and gastric arteries except along the first three or four mm. after their origin from the coeliac axis, in which part constriction was produced.

The Depression of the Freezing Points of Sodium and Calcium Chlorides. By F. E. E. Lamplough, M.A., Trinity College.

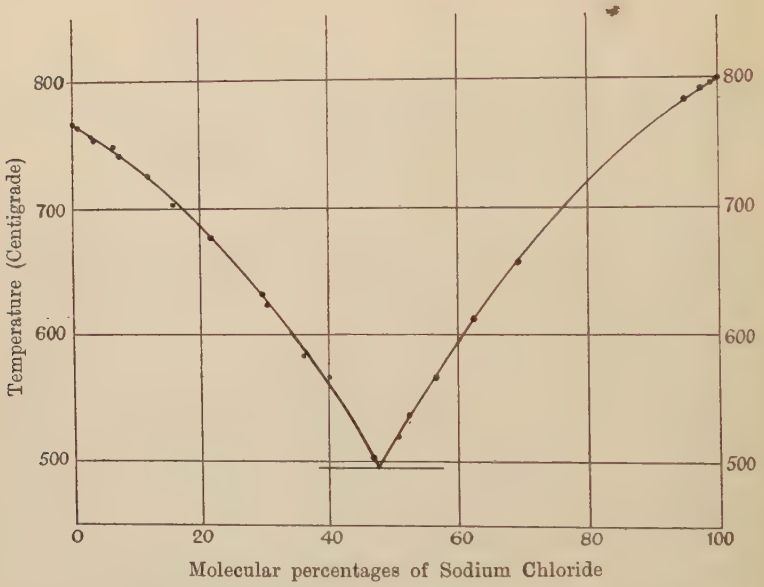
[*Read* 13 March 1911.]

Experiments have been made on the depression of freezing points of certain fused salts, in particular the chlorides of calcium and sodium. From 300 to 400 grams of the salt were fused in a large platinum crucible by a gas blow-pipe. The fused mass was kept in active circulation by a platinum paddle which was rotated by a small water motor. The temperature was measured by a platinum resistance thermometer used in conjunction with a Callendar recording pyrometer. The recorder was standardised by determining accurately with resistance box and bridge the temperature of the freezing points of sodium chloride and of some mixtures with potassium chloride.

Some experiments were first made with fused sodium carbonate, and later cryolite was used. The freezing point of the specimen of cryolite examined was 1004° C. and this was too high for convenience. A series of experiments were then made with fused calcium chloride as solvent. In all these experiments it was found necessary to introduce a nucleus of solid calcium chloride to prevent superfusion of the liquid. This was done by making two experiments on the cooling of each liquid mixture, and during the second experiment as the temperature approached the freezing point of the liquid an iron wire was introduced through the lid of the crucible to touch the surface of the liquid and was then withdrawn, this being repeated until freezing had commenced. The following values were obtained for the molecular depression of the freezing point of calcium chloride calculated for solutions containing in 100 grams of the solvent ·025 gram molecular weights of the following substances:

Strontium chloride	240
Lithium chloride	340
Sodium chloride	362
Barium chloride	380
Potassium chloride	448

In the case of sodium chloride determinations were made of the freezing points of various mixtures of the two salts from 100°/₀ calcium chloride to 100°/₀ sodium chloride, and in the diagram are given the results obtained. From this curve, with eutectic



point at the intersection of two freezing point curves, it is obvious that the two salts do not form any continuous series of solid solutions, and in all probability the pure salts crystallise out from the liquid mixtures. The above numbers are not very regular, and to interpret them a knowledge of the latent heat of solidification of calcium chloride would be necessary. There are great difficulties in the determination of this quantity at such temperatures as the freezing point of calcium chloride, 767° C., but it is hoped that these may be overcome at some future time.

In another series of experiments fused sodium chloride was used as solvent, the dissolved salts being either sodium salts or chlorides. In these experiments also it was found necessary to promote the formation of the solid phase by introduction of a nucleus. The weight of sodium chloride used was in most cases 351 grams (six gram-molecules). The following tables give some of the results obtained for the freezing points of solutions of the different salts in sodium chloride.

Weight of sodium chloride in each case 351 gms. Freezing point of sodium chloride taken as 800° C.

Potassium chloride		Calcium chloride	
gm. mols.	Temp. C.	gm. mols.	Temp. C.
·020	799	·019	799
·040	798	·038	798
·081	796·5	·078	796
·188	791	·159	792
·403	781	·319	783·7

Lithium chloride		Barium chloride	
gm. mols.	Temp. C.	gm. mols.	Temp. C.
·020	799	·027	798·6
·060	797·5	·054	796·7
·140	793	·108	793·7
·322	785	·161	790
		·215	787

Similar results were obtained with other salts, showing in each case that the depression of freezing point was within experimental error proportional to the mass of salt dissolved, and if any variation from this law due to ionization existed in dilute solutions it could not be detected by this method of measuring temperature differences.

The following values for the molecular depressions of the freezing point of sodium chloride are calculated in each case for a concentration of ·05 gram-mols. of dissolved substance in 100 grams of sodium chloride.

Salt dissolved	Molecular depression
Sodium bromide	81
Potassium chloride.....	166
Lithium chloride	164
Calcium chloride.....	180
Strontium chloride.....	176
Barium chloride	202
Sodium carbonate	180
Sodium sulphate.....	204

With the exception of sodium bromide it may be concluded that the molecular aggregation of the various salts is the same. Following on this preliminary survey it is intended to determine if possible the latent heat of fusion of sodium chloride, and to determine the freezing points at very small concentrations by direct measurement of the resistance of the platinum thermometer.

Three determinations of the freezing point of different portions of the sodium chloride used in these experiments gave the values 799·58°, 799·53° and 799·49°—mean 799·53° C.

I am greatly indebted to Mr Heycock for experienced advice during the work and for his generosity in placing at my disposal the valuable apparatus used in the research.

PROCEEDINGS

OF THE

CAMBRIDGE PHILOSOPHICAL SOCIETY.

VOL. XVI. PART III.

[Easter Term 1911.]

A SHORT FLORA OF CAMBRIDGESHIRE, CHIEFLY FROM AN ECOLOGICAL STANDPOINT, WITH A HISTORY OF ITS CHIEF BOTANISTS.

By A. H. Evans, M.A., Clare College.

The Lower Cryptogams by the Rev. P. G. M. Rhodes, M.A., Pembroke College;

G. S. West, M.A., D.Sc., F.L.S., St John's College, and

F. T. Brooks, M.A., Gonville and Caius College.

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PREFACE.

THE following pages have been written with the intention of bringing the Flora of Cambridgeshire up to date, as Babington's work on the county was published as long ago as 1860; and also in the hope that they may be found useful by the workers at the Botany School of the University, and Field-Botanists in general, until a larger and more detailed work is issued.

The author, with the assistance of many kind friends, has been able to certify the continued existence of many rare species of plants in the district, as well as to add largely to the lists previously published; and he wishes to take this opportunity of expressing his warmest thanks, not only to his coadjutors, who have furnished the important articles on the Lower Cryptogams, but to his other helpers—especially Dr Moss, Curator of the Herbarium, and the Undergraduates who have formed the bulk of those taking part in the regular Botanical Expeditions.—Others will be found mentioned below, who have been specially concerned in the Botany of the County, but to these should be added Mr G. C. Druce of Oxford as well as Mr C. E. Salmon of Reigate, who has furnished much information on specimens in the Herbarium of the "Holmesdale Natural History Society." Finally we are indebted to Messrs H. and J. Groves for much help on the *Characeæ* of Cambridgeshire, the localities being in this case given fully, as they are in the genus *Potamogeton*, in the hope of stimulating further research.

The separate contributors to the Lower Cryptogams have been allowed a perfectly free hand, as the treatment best for the Phanerogams might not be equally suitable for these groups.

A. H. EVANS.

9 Harvey Road, Cambridge,
October 12*th*, 1911.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

A SHORT FLORA OF CAMBRIDGESHIRE, CHIEFLY FROM AN ECOLOGICAL STANDPOINT, WITH A HISTORY OF ITS CHIEF BOTANISTS.

By A. H. Evans, M.A., F.Z.S., Clare College.

I. CAMBRIDGESHIRE BOTANISTS.

In early times the county of Cambridge was exceptionally fortunate in its Botanists; but this might perhaps be expected to have been the case, as it includes within its boundaries one of the two most ancient seats of learning in Britain. Long, however, before a regular School of Botany was recognised by the formal appointment of a Professor in the University in the year 1724, the celebrated John Wray or Ray published at Cambridge a 12mo work entitled *Catalogus Plantarum circa Cantabrigiam nascentium*, which gave a selection of synonyms, and notes on the localities where the plants were found. This was issued in 1660, and was followed by an Appendix in 1663, and a second edition of the same, published by Peter Dent, a Cambridge apothecary, in 1685. Subsequently Ray, instead of preparing a new edition of his original work, thought it better to write a book on the plants of the whole of England, which appeared in 1670 (ed. 2, 1677), under the title of *Catalogus Plantarum Angliæ* (London, 12mo), while he furnished a list of Cambridgeshire plants by marking all such with the letter *C*. A list of the rarer species in the county contributed by Ray to Gibson's edition of Camden's *Britannia* in 1695 contains nothing new, but this is not astonishing when we consider that he left Cambridge in 1662.

In this way was laid a solid foundation for all future botanical work in the county, such being then amicably shared by the University and the town, but subsequently a fresh impetus was given to the study of this branch of science by the establishment of the Professorship of Botany by the former in 1724. The first

holder of the office, Richard Bradley, F.R.S., does not appear to have written on the plants of the district, but when John Martyn, F.R.S., of Emmanuel College, was recalled from London, where he had been engaged in lecturing, and succeeded to the chair in 1733, he had already written his *Methodus Plantarum circa Cantabrigiam nascentium* (London, 12mo, 1727). In his Introduction to the *Flora of Cambridgeshire*, Professor Babington tells us that this work appears never to have been regularly published, and that it was prepared for the use of students attending Martyn's first course of botanical lectures at Cambridge, but, if so, he must have been able to predict his future appointment no less than six years before his election. In the *Methodus* he included the whole of the work of Ray and Dent, accepted the generic characters in the former's *Methodus emendata et aucta*, and other publications, and, in place of an alphabetical order, arranged the whole according to the system of classification approved in his time, but he mentions no new plants. A second edition was projected, but only a sheet and a half were printed. The third Professor was Thomas Martyn, of Sidney College, elected in 1761, who followed in his father's steps by issuing in 1763 his 8vo *Plantæ Cantabrigienses*, coupled with what he termed *Herbationes Cantabrigienses* (or thirteen botanical excursions), and therein he made a fresh advance by using the Linnean classification and nomenclature. In the body of the work only the names of the plants are given.

Our fourth Professor was J. S. Henslow, of St John's College, elected in 1825, who was a great lover of field-botany, and added much to our knowledge of local plants. He drew up in 1829 *A Catalogue of British Plants, arranged according to the Natural System, with the Synonyms of De Candolle, Smith and Lindley* (12mo), and italicized all plants not found in the county. In a second edition he improved upon this by adding the synonyms of Hooker, and denoting Cambridgeshire species by the letter *c*. Constant references to his records are to be found in the pages of the *Flora of Cambridgeshire*, published in 1860 by our fifth Professor, C. C. Babington, F.R.S., of St John's College, who succeeded to the post in 1861, and held it till his death in 1895. Still more celebrated than his predecessor, he was an authority not only on the plants of our district, but also on those of Britain in general; while his work both in the herbarium and in the field has left a lasting impression upon botany in the University. His *Manual of British Botany* has gone through nine editions, the last having been revised and augmented by Messrs H. and J. Groves. In the *Flora of Cambridgeshire* we find details of the habitats of the various species of plants, with references in particular to the oldest authorities, while the introductory chapters and the appendices add to the value of the book. Owing to pressure

of other work Babington had to rely to a large extent on information gathered from his correspondents, who were comparatively few in some parts of the county; and this accounts for the scanty records from those parts, and the entire omission from the lists of *Cardamine amara*, *Silene conica*, *Digitalis purpurea* and other noticeable species.

But it must be remembered that it was during the latter part of the Professor's tenure of office that a great impetus was given to the study of botany, in a new direction, by the discoveries of foreign savants with regard to the internal structure and physiology of plants, which were followed up by workers in England, and Cambridge in particular—among whom we must not omit to mention the name of our well-known authority, Dr Walter Gardiner, who practically refounded the Museum of Botany, in collaboration with Mr M. C. Potter, about 1885, and has written a full account of its foundation (by Henslow) and its re-establishment (Camb. Univ. Press, 1904). Field-work was for a time overshadowed by that of the laboratory and class-room, and to some extent its value was under-estimated. Babington, as one of the old school, must have found it very hard work to keep pace with the new discoveries, and though Dr Vines (now Professor at Oxford) and Dr Francis Darwin, who is still with us, were at hand to give every assistance, it is certain that less time could be devoted to the herbarium and the field by the University authorities. Misled by appearances, many have thought that the pursuit of field-botany languished during this period, but such was by no means the case; it simply fell into the hands of those not officially connected with the Professorial staff, and many names might be given of those who did excellent work in Cambridgeshire during this "eclipse" period. It is sufficient here to mention the name of Mr Alfred Fryer of Chatteris, who from that place as a centre explored many of the least-known parts of the county and recorded many forms new to it or else of doubtful occurrence. In particular he was, and still is, a great authority on the genus *Potamogeton*. To Mr Arthur Bennett of Croydon, moreover, we owe a debt of unfailing gratitude, for the interest which he has always taken in our flora and our herbarium, and for the aid—constantly asked and never refused—which he has afforded to us all in so many cases, especially with regard to those critical forms, in the knowledge of which he is a past-master. We must here mention his 'Notes on Cambridgeshire Plants' (*Journal of Botany*, 1899, pp. 243—247), which acts as an appendix to W. West, Junr's paper of the same name in that *Journal* for 1898 (pp. 246—259), and an article on the plants of the Kirtling district by R. A. Pryor in the same periodical (1874, p. 22).

Even under the shadow of the laboratories, moreover, were men with their heart in field-work, such as Messrs Potter, Willis, Burkill, Hill, G. S. West, and Yapp, who were now rapidly coming to the front, and ensuring that in the long run field-botany should not suffer from its temporary sleep at the Museums, but wake again with renewed vigour. They have all left us to fill important posts in England or abroad, but with the death of Professor Babington came the recall to our assistance from Coopers Hill of one of the most brilliant of Cambridge scientific men, H. Marshall Ward, F.R.S., of Christ's College. He was appointed Professor in 1895, and, although hampered greatly by his duties in connexion with the building of the splendid new quarters for the Botanical Department, his laboratory work and teaching, he nevertheless found time to set on foot a scheme for collecting further material for a new Flora of Cambridgeshire, and encouraged all those presently working in that line to redouble their efforts. Himself a very great authority on cryptogams and especially microscopic fungi, on grasses and trees, he had published many important papers and books on those subjects, and was exceptionally qualified to lead the way in every part of our branch of science, so that the loss to Cambridge botany, when his career was unfortunately cut short by his death in 1906, is not easy to estimate.

Fortunately for us our present Professor, A. C. Seward, F.R.S., of St John's College, though primarily devoted to the Palæontological side of Botany, at once shewed himself fully alive to the importance of field-work, and, fearing that his other duties would not allow him time to supervise it to his satisfaction, gave practical proof of his interest in the subject by selecting for the post of Curator of the Herbarium Dr C. E. Moss (formerly of the Manchester University, now of Emmanuel College), who happily combines the qualities for the indoor and outdoor lines, and is known as an admirable worker in the field, both from the systematic and from the ecological standpoints. Under his guidance our botanical expeditions have taken a new lease of life, and the more critical forms of plants are being studied to the greatest advantage. Mr A. G. Tansley, of Trinity College, who joined the botanical staff about the same time, is another leading authority on ecological botany, and is heartily co-operating with us in the work. We expect also that the various members of the staff of the Botany School will render efficient aid, as far as their occupations will allow; and here we may especially mention Mr R. P. Gregory, of St John's College—whose mother, Mrs Gregory of Weston-super-Mare, has come to reside in Cambridge, and is working more particularly at the Violet group—and Mr F. T. Brooks of Gonville and Caius College, who is contributing to this work the article on Fungi. The Rev. P. G. M. Rhodes, of Pembroke

College, has, moreover, provided us with lists of the Mosses and Lichens, while Mr Arthur Bennett's aid must again be particularly mentioned here, as must also that of Mr Alfred Fryer, Messrs H. and J. Groves and Dr G. S. West, above mentioned, for the genus Potamogeton, the Characeæ and the Algæ respectively. Mr C. E. Salmon of Reigate, Mr G. Goode, the Secretary of the Watson Botanical Exchange Club, and Mr A. Shrubbs have also kindly furnished information for the lists below.

It will thus be seen that we have no lack of workers in field-botany at the present time, and that much may be hoped for the future; but it is now our duty to recall the names of the older botanists, other than official. Of these the earliest after Peter Dent is Israel Lyons, Junr, who published in 1763 at London an 8vo *Fasciculus Plantarum circa Cantabrigiam nascentium, quæ post Rajam observatæ fuere*; but his successor, Richard Relhan, chaplain of King's College, was a much more eminent botanist, and published in 8vo a full *Flora Cantabrigiensis* at Cambridge in 1785. He subsequently brought out three supplements dated 1786, 1788 and 1793, while two further editions of the whole work appeared in 1802 and 1820. Consequently Relhan not only brought our Flora up to date in the early twenties, but his time may be considered as the starting point of the modern period of our botany; for he not only included the records of those who wrote before him, gave generic characters, diagnoses of species, a selection of synonyms, trivial names, localities and times of flowering of the plants, but also furnished an account of the Musci, Hepaticæ, Algæ, Fungi and Lichenes. The importance of the last fact will be recognised when we note that Babington in his later work entirely omits these groups; and that those who are preparing the present lists have had practically no previous work except that of Relhan to guide them in this respect, if we except Dr West's own paper on the Algæ in the *Journal of Botany* for 1899 and some work by Mr Larbalestier on the Lichenes.

Mr H. C. Watson's *New Botanist's Guide* (1835—1837) adds a certain amount to our knowledge of Cambridgeshire plants, for information on which he was greatly indebted to the Rev. W. H. Coleman, of St John's College. Mr G. S. Gibson's 'Flora of the neighbourhood of Saffron Walden' (*Phytologist*, Vol. I., *passim*) contains a few notices of Cambridgeshire plants, and Babington acknowledges in the *Flora of Cambridgeshire* the assistance of many correspondents, who cannot be given in detail here, but among whom the Rev. W. W. Newbould of Comberton, and Mr S. W. Wanton, of St John's College, stand out prominently.

II. THE PHYSICAL FEATURES OF CAMBRIDGESHIRE, WITH ITS GEOLOGICAL FORMATIONS, AND THEIR ATTENDANT FLORA.

The county of Cambridge has still an extensive flora, with an abundance of interesting and uncommon plants, though the drainage of the low-lying fen-lands has been the cause of the disappearance of many of the rarer species, details concerning which will be found in the first of the succeeding lists. On these drained and cultivated fen-lands there has been little attempt at afforestation; thus they still present in most parts the aspect of cultivated open flats divided into sections by wider or narrower water-courses, to which the names of lodes or dikes are given according to their size. Shelter strips of poplars are in many places a conspicuous feature, as are the pollard willows which commonly line the banks of the streams, while near the villages there is no lack of hedges of hawthorn and the like. The remainder of the county is fairly well timbered, though many of the existing woods have been planted, and the vast bulk of the ancient forests have disappeared. Yet several of the existing woods on the boulder clay, the chalk, and the greensand, do possess some primitive characters, although modified to a certain extent by sylviculture, and probably represent the remains of the primæval forests of the county, which are vouched for by the remains of oaks and so forth disinterred from the base of the various recent alluvial or peaty deposits.

Plants which grow at great altitudes or are peculiar to upland moors cannot of course be expected in so flat a district, where the Gog-Magog Hills (240 ft) and Madingley Hill (175 ft) are the chief eminences that break the landscape, but the chalk downs that traverse the county from east to west, and the grassy expanse of Newmarket Heath, enable us to add to our list many species which would otherwise be lacking.

The rivers Cam, Nene, Ouse and their tributaries make Cambridgeshire a well-watered area; but there is a marked absence of any large sheets of water since the disappearance of Soham, Stretham, Benwick and other "Meres," though there is a certain amount of compensation to the botanist in the presence of

patches of marsh-land still remaining in the midst of a well-executed scheme of drainage. The only really extensive fen is that well known to exist at Wicken, and from this a mile or two of rough grassy or rushy pasture intersected by peat-holes stretches in the direction of Burwell and Reach. Thence to Waterbeach and Horningsey the Fens hardly exist except in name, and the same may be said of the northern division of the county, where we can only point to the Guyhirn washes, Chatteris Turf Fen and the so-called "Firelots" at Wimblington. An interesting piece of fen, however, occurs at Chippenham, and a still smaller area at Dernford near Shelford. The washes of the Cam are fast drying up.

Contrary to popular opinion, therefore, Cambridgeshire is by no means a land of sedge-fen and morass, but consists of a series of comparatively dry flats to the northward and of more elevated down-lands to the southward, the woods being chiefly confined to the latter portion of the county and seldom being of any great size. Estuarine plants are only to be found in the neighbourhood of Wisbech, on the tidal portion of the Nene.

Professor Babington, in his *Flora of Cambridgeshire* of 1860, divided the county into eight more or less arbitrary sections, but as his method threw parts of the fen-land and the chalk into different divisions, while it failed to keep the Gamlingay green-sand or the blown sand at Chippenham—with their peculiar flora—apart, we do not feel inclined to follow his lead. On the other hand Mr A. Wallis, who contributed an article on the Flora of the Cambridge district to Messrs Marr and Shipley's *Natural History of Cambridgeshire* in 1904, follows H. C. Watson in classifying the plants as British, English, Germanic, and Atlantic, but also classes them, with the exception of the estuarine species, as those of the Fen, Dry Soil, Meadow, or Shade Associations. The latter method is perhaps more suited to the modern ideas of Ecology than that of Babington, but can hardly be commended, for, to mention only two objections, it combines the chalk to a certain extent with the gravels, and takes no special heed of the boulder or other clays*.

On the whole it seems best to follow to a great extent the geological formations of our district, and to concern ourselves only with the following divisions:—

1. Alluvium, Peat and River Gravels.
2. Clays (Oxford Clay, Ampthill Clay, Kimmeridge Clay, and Gault)—excluding the Boulder Clay.
3. Chalk.

* Since this was written, Professor and Mrs McKenny Hughes have published an admirable account of the Geography of Cambridgeshire, including the Geology, Natural History and so forth, which will be found most useful by all interested in the county. (University Press, 1909.)

4. Lower Greensand of Gamlingay.
5. Boulder Clay.
6. Blown sand over chalk (as at Chippenham and Kennett).

It may here be stated that we include in the county the small detached piece of Suffolk adjoining Newmarket, as did Professor Babington.

1. Alluvium, Peat, etc.* This large division fills a great part of the north of the county, and, besides the present fen-land proper, includes the ancient fen-land reaching nearly from Peterborough to St Ives, and an extensive area of marine silt drained by the rivers Nene and Ouse, from Wisbech to the neighbourhood of Ely. Consequently the plants may be roughly apportioned to three groups: (1) those which are chiefly or entirely maritime, (2) those correlated with drier soil, with no special attraction to chalk, heavy clay or loose sand, and (3) those of the peat and its vicinity. Our alkaline peat exhibits a very different Flora to the acid peat of other places.

Maritime plants are only found around Wisbech, though the influence of the tide is shown in another direction as near the county boundary as Denver in Norfolk. An exception must, moreover, be made in the case of *Scirpus maritimus* and *Aster Tripolium*, which occur as high up the rivers as Sutton, and in the case of the former, as Upware, while *Apium graveolens* and other species may denote the former presence of salt water in places now far inland. Among these maritime plants we still possess at least *Spergularia salina* b. *media*, *S. marginata*, *Aster Tripolium*, *Statice maritima*, *Glaux maritima*, *Plantago maritima*, *Beta maritima*, *Atriplex portulacoides*, *Suæda maritima*, *Zostera marina* c. *angustifolia*, *Glyceria maritima*, *G. distans* and *Triticum pungens*. Others, such as *Frankenia lævis*, *Limonium vulgare*, *L. reticulatum* and *Atriplex pedunculata*, have now apparently disappeared, owing to the drainage of the salt marshes at Foul Anchor about a century ago.

For the plants of the second group, which presents no peculiar features, reference may be made to the general list below, but in the third group are many fen plants which are rare and of more than ordinary interest. A "fen" in Cambridgeshire means a sedge-fen—if it has not been drained, and a sedge-fen means a fen covered with a dense growth of *Cladium Mariscus*, with a lower carpet of *Carices* and such grasses as *Agrostis alba* and *Molinia cærulea*. *Phragmites communis* edges or chokes the smaller dikes,

* Where the Survey maps indicate the Jurassic or Cretaceous clays, or the lighter formations, such as lower greensand or chalk, there are commonly superficial deposits, which are so thick as to give a character to the soil quite irrespective of the underlying "solid geology."

and also intrudes among the *Cladium*, which responds by encroaching upon the *Phragmites* in the shallower water-courses. *Juncus subnodulosus*, *Calamagrostis epigejos* and *C. lanceolata* form a considerable portion of the vegetation of Wicken sedge-fen (and were doubtless commoner elsewhere in olden time). *Rhamnus catharticus* and *R. frangula* are the shrubs proper to this fen, with some willows, brambles and small hawthorns; *Lathyrus palustris*, *Lythrum Salicaria*, *Peucedanum palustre*, *Lysimachia vulgaris*, and *Cnicus pratensis* are specially conspicuous, while *Lastrea Thelypteris* occurs here and there in profusion. Others of the rarer species are *Viola stagnina*, *Stellaria palustris*, *Sium latifolium*, *Utricularia vulgaris*, *U. minor*, *Myrica Gale*, *Liparis Loeselii*, *Helleborine longifolia*, *Sparganium minimum*, and *Butomus umbellatus*, besides several members of the genera *Potamogeton* and *Carex* and of the *Characeæ*. *Carex paradoxa* and *Nitella tenuissima* may be more particularly mentioned. *Senecio paludosus*, *S. palustris*, and *Sonchus palustris* have not been found for many years, as will be seen below, nor does it appear that the two latter ever grew at Wicken. From the records of Ray, Relhan and others the very wet neighbourhood of Stretham seems to have possessed a particularly rich flora, and the same may be said of Hinton Moor near Cambridge, in the times of old. But it may be suspected that in still earlier days, and also in less accessible places, many of the rarer species were unnoticed. The valley fen at Chippenham still furnishes *Liparis Loeselii*, *Drosera rotundifolia*, and *Selinum Carvifolia*, while it is a well-known locality for other plants by no means common in the district.

2. Clays, other than Boulder Clay.

These do not form a continuous area, as will be seen from the Survey map; they are found as patches of Oxford and Ampthill Clay west of Gamlingay, near Longstanton, and elsewhere; as similar patches of Kimmeridge Clay situated for the most part on the "islands" or eminences of the fen country; and as considerable stretches of gault in various places along a line running in a north-easterly and south-westerly direction. The flora of this division has no very peculiar features.

3. Chalk. This division occupies the county between Newmarket and Royston; it is of considerable width throughout, and contains the main uplands of Cambridgeshire, of which the best known are the Gog-Magog Hills to the southward of the town of Cambridge. It is barely interrupted by a few areas of gravel, chiefly in the valleys of streams, and is marked by two long dykes of prehistoric date with high banks, near Fulbourn and Newmarket, Fleam and the Devil's Dyke respectively. Many of our rarest

plants are to be found in this division, among which especial attention may be drawn to *Anemone Pulsatilla*, *Linum perenne*, *Seseli Libanotis*, *Carum Bulbocastanum*, *Senecio integrifolius*, *Hypochœris maculata*, *Orobanche elatior*, *Muscari racemosum*, and *Carex ericetorum*; the orchids *Cephalanthera grandiflora*, *Orchis ustulata*, *Ophrys apifera* and *O. muscifera* still occur, though *O. sphegodes* and probably *Herminium monarchis* are now extinct; while a large number of species peculiar to chalk or with a preference for dry soils complete the list. *Onobrychis viciæfolia* is a favourite crop in these parts, and is almost as strictly limited to them in Cambridgeshire, as *Fagopyrum sagittatum* is to the fen country.

4. Greensand. In this division we may pass over the small patches of the Lower Greensand in the Isle of Ely and near Cottenham, and devote ourselves to the tract stretching from Gamlingay towards Sandy, where alone we find plants of a very different type to those of the rest of the county. The presence of some of these, such as *Teesdalia nudicaulis*, *Trifolium subterraneum*, *T. scabrum*, *Ornithopus perpusillus* and *Galium saxatile* is apparently due to the comparatively dry nature of the soil and not to the fact of it being composed of greensand, as they occur also eastward on the blown sand near Chippenham and Mildenhall; but a considerable list may be formed of plants few of which probably ever grew in Cambridgeshire much outside of the limits of the Gamlingay tract. Among these are *Mœnchia erecta*, *Hypericum humifusum*, *Solidago Virgaurea*, *Gnaphalium sylvaticum*, *Arnoseris minima*, *Oxycoccos quadripetala*, *Erica Tetralix*, *E. cinerea*, *Digitalis purpurea*, *Quercus sessiliflora*, *Convallaria majalis*, *Narthecium Ossifragum*, *Rynchospora alba*, *Deschampsia flexuosa* and *Lycopodium inundatum*; but it is evident on inspection of the list that only in Cambridgeshire can we call them, for our purposes, peculiar to the greensand. Associated with these we have the trees *Tilia cordata*, *Pyrus Aucuparia* and the above-mentioned *Quercus sessiliflora*, while *Ulex europœus*, *Cytisus scoparius* and *Pteris aquilina* are conspicuous features of the district. The Bogs were drained by 1855.

5. Boulder Clay. This division is here kept separate from that including the other clay soils on account of the very different character of its flora. In the first place certain of our plants are practically confined to this formation, as *Pyrus torminalis*, *Cnicus eriophorus*, *Primula elatior*, *Melampyrum cristatum*, *M. pratense*, *Lamium Galeobdolon*, *Daphne Laureola*, *Helleborine media*, *Colchicum autumnale*, *Carex remota* and *C. pendula*. In the second place many of the rarer species are hardly found elsewhere or are much more plentiful on it, as *Lathyrus sylvestris*,

Genista tinctoria, Trifolium ochroleucon, Bupleurum rotundifolium, Caucalis daucoides, Serratula tinctoria, Linaria Elatine, L. spuria, Euphorbia platyphyllos, Iris fœtidissima, Paris quadrifolia, and so forth; so that its peculiarities are sufficiently obvious even to the uninitiated.

Omitting small detached patches, for which reference may be made to the Survey map, the Boulder Clay extends over three very considerable areas in the county, one from near Huntingdon and Swavesey southwards to Gamlingay and the Orwell district, reaching eastward to within about two miles of Cambridge; a second running not quite continuously from Chishall near Royston to Linton; and a third hardly separated from the last-named, which extends from the east of Linton in a north-easterly direction along the higher ground towards and past Newmarket.

6. Blown sand. This division, mainly in the parish of Chippenham, begins between Fordham and Freckenham and extends past Chippenham village as far as Kennett. Part of it is cultivated, and part consists of sandy warrens, similar to those in the neighbouring districts of Norfolk and Suffolk, while the valley fen at Chippenham is in close connexion with it. Here, as on the Cretaceous sands of Gamlingay, *Ulex europœus, Cytisus scoparius* and *Pteris aquilina* are abundant, several of the less common species of *Trifolium, Ornithopus perpusillus* and *Calluna vulgaris* re-appear, while *Teesdalia nudicaulis* and several other rare species occur just outside the county. Of the plants which are not uncommon in this district, but are hardly ever or never found elsewhere in Cambridgeshire, the chief are *Silene conica, S. Otites, Medicago sylvestris, M. falcata, M. minima*; *Galium anglicum* also was recorded by Babington from the Park wall at Chippenham, and *Apera interrupta* is moderately plentiful. The last-named, however, was also found in 1855 at Pampisford near Cambridge.

With regard to the more critical forms of plants in general a considerable amount of work has been done, and specimens have been submitted to well-known authorities, whose assistance—and especially that so ungrudgingly given by Mr Alfred Fryer of Chatteris and Mr Arthur Bennett of Croydon—we must here most gratefully acknowledge; but in all probability further investigation will increase our lists and greatly add to the value of a new general Flora of Cambridgeshire, which it is intended to publish before many years have elapsed.

We may now proceed to consider the lists of plants stated to be lost or unknown in the county by Professor Babington in Appendices IX and X of his *Flora of Cambridgeshire.*

Of the plants reported to be lost, the following are still to be found: *Thlaspi arvense, Geranium rotundifolium, Lathyrus Nissolia, Pyrus torminalis, Sedum Telephium, S. album, Lactuca saligna, Senecio viscosus, Beta maritima, Polygonum minus, Salix purpurea, Colchicum autumnale, Setaria viridis, Phleum arenarium*; of those said to be probably extirpated we still have *Myosurus minimus, Œnanthe silaifolia, Kentranthus ruber, Limosella aquatica, Veronica spicata, Myrica Gale* and *Liparis Loeselii*. On the other hand many species—*Senecio paludosus* in particular—have not been seen for a considerable period.

Of plants said to be unknown in the county we have *Lychnis dioica, Digitalis purpurea, Festuca duriuscula, Tragopogon pratense, Epilobium angustifolium, Lepidium Smithii, Zostera marina* c. *angustifolia, Cardamine amara, Sagina maritima* d. *densa, Quercus sessiliflora, Teesdalia nudicaulis, Vicia lathyroides*, and possibly *Anagallis fœmina*.

III. ANNOTATED LIST OF SOME OF THE RARER PLANTS, MANY OF WHICH ARE NOW EXTINCT.

1. *Roemeria hybrida*, DC. This Poppy was at one time frequently found in the chalky fields lying between Reach, Burwell and Swaffham Prior. Judging from specimens in the Winch Herbarium of the Linnean Society and that of the Philosophical Society of York (Henslow) it was not extirpated before 1835, while the dates reach back to 1820. Probably the plant was introduced with agricultural seeds, and probably also it occurred in the district before our earliest record and after our latest. Babington records it on his own authority, and does not include it in his list of lost plants in 1860; but there seems to be no sure evidence of its maintaining itself to a later date than 1835.

2. *Arabis Turrita*, L. Ray does not mention this species, which is first recorded by T. Martyn in 1763 as growing on old walls about Trinity and St John's Colleges. It is still found in the grounds of the latter College, though in its present locality it may have been introduced more recently than in its former.

3. *Sisymbrium Irio*, L. This plant, always of interest on account of the story of its appearance after the Great Fire of London, was reported from Barnwell in 1818 by Mr Job Watson, of Hemingford, Hunts., and by Mr W. Skrimshire from Wisbech, prior to 1802. It is a species that usually lingers for a long time when it has once taken to the ground, as at Berwick-on-Tweed in the present day; and we should have expected further records from the county, unless it was a temporary casual of the rubbish-heap.

4. *Lepidium latifolium*, L. This Pepperwort is recorded from Leverington near Wisbech by Mr Skrimshire, but has never been noticed since his time. The locality, being near the sea, is natural, and there is no more reason to doubt this ancient record than those of later date, while modern lists, rightly or wrongly, consider the plant a true native.

5. *Frankenia lævis*, L. This plant was recorded by Professor T. Martyn from the salt marshes at Tydd Gout, near Wisbech.

These marshes were, however, drained before 1860, and *Frankenia* seems to have been extinct long before that date, although it is still fairly plentiful on the Wash, no further away than Holme, near Hunstanton.

6. *Hypericum elodes*, L. This species used to grow in the bogs at Gamlingay, but does not seem ever to have occurred in the Fens. The late W. West, junr, writing in 1898 (*Journ. Bot.*, July, 1898), says that it "grew until recently by the stream near the site of the old bog at Gamlingay, but I could not find it in 1894." We have, however, no means of knowing what "recently" means in this connexion, but from a letter of Babington to A. G. More (*Memorials &c. of Babington*, p. 344), we learn that the plant had not vanished in 1860. Perhaps stray individuals lingered to a later date.

7. *Vicia sylvatica*, L. Relhan's record of "Hall Wood, near Wood Ditton" still stands alone for the county. The wood was cut down long ago, but the specimen sent thence by the Rev. John Hemsted is worth noticing, as having been figured in Sir J. E. Smith's *English Botany* (1792). The plant occurs in the adjoining county of Hertfordshire.

8. *Drosera anglica*, Huds. Recorded of old from Sawston and Hinton Moors by Relhan. From a note kindly communicated by Mr C. E. Salmon, we find that there is a specimen from Whittlesey in the collection of J. A. Power, now in the Herbarium of the Holmesdale Natural History Society at Reigate, but it is more than likely that the habitat was in the direction of Whittlesey Mere, and therefore not in Cambridgeshire.

9. *D. longifolia*, L. Ray gives Hinton Moor as a locality for this species, Relhan gives Teversham and Sawston Moors. Without the specimens it is impossible to speak with certainty; but this species might possibly have been confounded with the last-named, though the "moors" before they were drained were as likely to have furnished it as *D. anglica*. It may be noted that *D. rotundifolia* is still found in the county at Chippenham.

10. *Lythrum Hyssopifolia*, L. Babington's own records are from the neighbourhood of Cambridge and Chippenham, while he gives others from Teversham, Hinton, Chesterton, Histon, Oakington, Madingley and Ely, taken from his predecessors or coadjutors. Newmarket must be added on the strength of a specimen in the Winch Herbarium of the Linnean Society, as we are informed by Mr Arthur Bennett; but not one of the records gives any idea of

the *status* of the plant, or furnishes any indication of whether it was a casual or not.

11. *Cicuta virosa*, L. The old record of Professor J. Martyn gave as the locality a spot between Ely and Prickwillow, and we are again indebted to Mr Bennett for the information that the Rev. J. Dalton's collection in the Herbarium of the York Philosophical Society contains a specimen gathered by Dr Goodenough in 1786. We are still unable to discover the plant in the county —as was Babington—but live in hopes of doing so, for Professor Yapp of Aberystwith tells us that he found it so near to our boundaries as Stalode Wash in Norfolk in 1908.

12. *Caucalis latifolia*, L. Formerly abundant in the county, now exceedingly rare (Babington in 1860). No doubt a casual of corn fields, as it is considered in the London Catalogue; but the fact remains that *C. daucoides*, though local, is still not uncommon, while, for no apparent reason, its congener has disappeared.

13. *Gnaphalium luteo-album*, L. As the figure in Sir J. E. Smith's *English Botany* was taken from a specimen sent by Relhan from between Hauxton and Little Shelford, we can certainly claim the plant for the county; but we have only Relhan's record.

14. *Pulicaria vulgaris*, Gaertn. Judging from the account in Babington's *Flora of Cambridgeshire*, this species was still to be found in or about 1860; but we have been quite unable to discover even a single specimen in the county, and the plant seems to have become extinct in Cambridgeshire, as there is reason to suppose is the case in more than one place in southern England. It loves grassy road-sides and commons and is therefore easily extirpated, especially by the builder.

15. *Senecio paludosus*, L. This species has been found in the counties of Norfolk, Suffolk, Cambridge and Lincoln, as will be seen from Mr Arthur Bennett's article in the *Transactions of the Norfolk and Norwich Society* (vol. VI, p. 457), where the details are fully given. Mr Bennett has kindly allowed me to use his MS. notes, from which many of the following facts have been taken.

The first record for Cambridgeshire seems to be that of Ray in his *Catalogus Plantarum circa Cantabrigiam nascentium*, p. 37 (1660).

In the Wilkinson collection belonging to the York Philosophical Society is a specimen from the county, gathered in 1800. The Rev. J. Holme of Peterhouse, subsequently Vicar of Cherry Hinton and Rector of Freckenham, is responsible for at least six

of those still in existence. One of these is that in the Wilkinson Herbarium at York, one is in the collection of Mr Arthur Bennett, one in that of the Holmesdale Natural History Society at Reigate.

All of them were gathered between 1800 and 1825 in Wicken Fen. Professor Henslow found the plant about three miles below Ely in 1833, and Professor Babington saw one of the specimens. Another in the Salt Herbarium at Sheffield ("Ely, 31.7.1833") may have been gathered by Henslow or by Mr W. Marshall of Ely, who gives Padnal Fen and Barraway Washes as localities somewhere about the same time.

One of Marshall's specimens is in Mr F. J. Hanbury's collection, a second cannot now be traced.

In 1857 Babington saw a plant in Wicken Fen, which may have been that transplanted later into the Botanic Garden at Cambridge. Two specimens were gathered, now in Babington's Herbarium.

Between 1878 and 1883 Mr Bennett is able to state, on the authority of Mr Wilton of Soham, that eleven specimens were discovered, and there our information comes to an end, while it is to be feared that since 1883 this *Senecio* has become extinct.

Two undated specimens, gathered by Dawson Turner in the county, are in the Winch Herbarium of the Linnean Society; Ray states that he found the plant "in many places about the Fens, as by a great ditch side near Stretham Ferry"; T. Martyn (1763) gives Chatteris; and Relhan (1785) Littleport and Burwell Fen as localities.

16. *Senecio palustris*, Hook. The first record of this plant in Cambridgeshire is that of Ray in his *Catalogus Plantarum circa Cantabrigiam nascentium* of 1660. He found it about March and Chatteris. Relhan reports it in the year 1820 from "a ditch at the edge of the moor next to the Park at Chippenham." Considering that it was a less uncommon species than *S. paludosus*, and not confined to the Eastern Counties, it is disappointing to find that we have no later record than those noted above; for that given by Babington (*Flora of Cambridgeshire*, p. 129) on the authority of Mr W. Marshall of Ely is stated in that gentleman's own notes to have been due to some error. See *Journ. of Botany*, 1899, p. 244.

17. *Arnoseris minima*, Schweigg. and Koerte. Professor Babington, writing in 1860, records this species from fields on the old Heath at Gamlingay, but it was not again noticed, as far as it is possible to ascertain, until 1910, 1911, when Mr N. Simpson of Trinity College and Mr A. H. Evans each found a single specimen on the site of the old Heath.

18. *Crepis fœtida*, L. Recorded from several localities in the county in Babington's *Flora of Cambridgeshire*. They need not be given in detail, but it must be noted that Mr Arthur Bennett has examined a specimen dated 1854 in the Herbarium of the York Philosophical Society, and has thus vouched for the Professor's identification of the plant, though it does not appear to have been found since 1860.

19. *Sonchus palustris*, L. We may perhaps assume, from our knowledge of the Fens of old, that this species occurred in several localities in early days; but even Mr Israel Lyons, writing in 1763 on plants observed round Cambridge after the time of Ray, can only record it from "near Stretham Ferry." In the Hailstone Herbarium at York, however, Mr Arthur Bennett found a specimen from Bottisham Fen dated 1839, and another gathered in 1843 "opposite the Knave of Clubs Alehouse" near Bottisham, the last known from the county.

20. *Oxycoccos quadripetala*, Gilib. The Cranberry, though once abundant, seems to have been restricted to the Gamlingay Bogs, and in 1859 was confined to "one small spot" (Babington). It is now extinct in that locality.

21. *Erica cinerea*, L. This species, unlike *E. Tetralix* and *Calluna vulgaris*, has not been found since 1860, when Babington records it in the *Flora of Cambridgeshire* from Gamlingay.

22. *Limonium reticulatum*, Mill. Found at Tydd Marsh by Mr Skrimshire, about 1820, and also by the Rev. J. Hemsted, below Wisbech, whence Mr Algernon Peckover reports it shortly before 1860. A specimen dated Sept. 1796 is in the Herbarium at the British Museum and is marked T. Sowerby. The plant has quite disappeared from the county though still common in Norfolk. *L. vulgare* may still linger at Wisbech.

23. *Lysimachia nemorum*, L. "Hall Wood, Wood Ditton," the locality given by Relhan, was already cut down when Babington wrote in 1860, but the botanists of the county are still in hopes of finding the plant elsewhere.

24. *Veronica spicata*, L. This species, confined to the counties of Cambridge, Norfolk and Suffolk, used to be found in various places on Newmarket Heath and the immediate vicinity. Now it is possibly confined to one or two, though this cannot be positively asserted; but that it still exists may be taken for certain. Owing to the grass among which it grows being constantly cut, the plant may not flower every year, but about a hundred spikes were seen a few years ago. Mr Arthur Bennett

states, moreover, that he possesses an old specimen from Litlington, near Royston.

Mr R. B. Smart's record from near Fleam Dyke has never been confirmed.

25. *Teucrium Scordium*, L. The Water Germander is still found near Upware and at Roswell Pits, Ely, but has presently disappeared from Sutton Gault, Horseway near Chatteris and localities between Cambridge and Ely given in Babington's *Flora of Cambridgeshire*. It grows in pits or on banks of ditches, and is hardly to be called a fen plant.

26. *Chenopodium urbicum*, L. Unlike *C. murale* and *C. hybridum*, which have been re-found recently, this species is only known to us by the records of Relhan from Barnwell, Coton and Cottenham, and of Lyons from Hinton.

27. *Atriplex littoralis*, L.
28. *A. pedunculata*, L. } Neither of these plants can now be found near Wisbech, but whereas the former is still mentioned as present in Babington's *Flora of Cambridgeshire* (1860) the later only dates up to about 1830.

29. *Urtica pilulifera*, L. (*b*) *Dodartii* (L.). This alien and casual species has never been found in the county since it was discovered near Wisbech by Dr Jermyn and Upwell by the Rev. L. Jenyns.

30. *Myrica Gale*, L. Professor Babington considered that the Bog-Myrtle was destroyed by drainage and cultivation before 1850, but in this he was in error, as it still grows in two spots in Wicken Fen, and Mr Alfred Fryer saw a small patch in the "Firelots" near Wimblington in 1884 which was still there in 1892.

31. *Malaxis paludosa*, Sw. Hinton Moor, an old station for this species, was drained long before Babington wrote, but he records this Orchis from "Bogs, Gamlingay, formerly very abundant, nearly extirpated in 1855." This constitutes the latest record.

32. *Liparis Loeselii*, Rich. This species must have disappeared from Ray's station on Hinton Moor at the same period as *Malaxis*, and no doubt from Teversham Moor at about the same time. It is not likely now to be re-discovered at Fulbourn or Sawston, whence Relhan records it, or where Henslow found it at Bottisham Fen; but it still occurs in very small quantity in Chippenham and Wicken Fens, though Babington considered it extinct by 1836. Near Reach it may possibly still exist, judging

from the condition of some parts of that district. Mr Arthur Bennett has seen a specimen gathered long ago at Gamlingay by J. A. Power which is now in the Herbarium of the Holmesdale Nat. Hist. Soc. at Reigate. (Cf. *Trans. Norf. and Norw. N. H. Soc.* 1902, p. 335).

33. *Ophrys sphegodes*, Mill. Babington found this plant near Abington, May 24, 1837, older records being from near Bartlow, Hildersham and Shelford, but the disappearance of balks or wide grassy paths between small holdings or between fields, has probably been the cause of the extirpation of this Orchis, which is now never found in the county. (Cf. *Memorials &c. of Babington*, p. 88.)

34. *Fritillaria Meleagris*, L. Not recorded for the county, except by Relhan from Westhoe near Linton. If his plant was not the outcast of a garden, this species might still be rediscovered, as will be seen from the case of the next.

35. *Colchicum autumnale*, L. This species was only known to Babington as reported by Relhan "in a close on the south side of Mr Eaton's house at Wood Ditton." If the exact position of this close could be ascertained, the plant might be once more found there, as on August 17th, 1908, Mr R. L. Wormald of Weston Colville shewed a patch of it to a small company of Cambridge botanists in a wood near that village, and told them that he had picked the flowers there for ten or fifteen years. We have therefore to thank Mr Wormald for this modern record.

36. *Narthecium Ossifragum*, Huds. Extinct at Gamlingay Bogs since Babington's time, so far as can be ascertained.

37. *Triglochin maritimum*, L. The same may be said of this plant as of the last, except that it grew on the river-side below Wisbech.

38. *Rynchospora alba*, Vahl. Babington considered that this species might still survive at Gamlingay in 1860, as he had found specimens there "very recently, but it has not been observed since."

IV. GENERAL LIST OF SPECIES.

In this list the London Catalogue (ed. 10) has been, in general, followed. Square brackets imply that a plant is doubtfully native either in Britain or at least in Cambridgeshire.

I. ANGIOSPERMÆ.

Dicotyledones.

RANUNCULACEÆ.

Clematis Vitalba L. 3, 5.
Thalictrum minus L.
(*a*) *collinum* (Wallr.) 3.
T. flavum L. 1, 2, 3.
(*c*) *rufinerve* (Lej. and Court) 1.
Anemone Pulsatilla L. 3. Found on the Furze Hills, Hildersham, where the surface soil is sandy, as well as on the barer chalk dykes.
A. nemorosa L. 3, 4, 5.
Myosurus minimus L. 1, 2, 3, 4.
Ranunculus circinatus Sibth. 1, 2, 3, 5.
R. fluitans Lam. 1, 2, 3, 6.
R. trichophyllus Chaix. 1, 2, 3, 5.
R. Drouetii (F. Schultz) 1, 2, 3, 5.
R. heterophyllus Weber, 1, 2, 3, 5.
R. peltatus Schrank.
(*d*) *floribundus* (Bab.) 5.
(*e*) *penicillatus* (Hiern.) 1.
[*R. Baudotii* Godr. 2.]
R. hederaceus L. 1, 2, 3, 4, 5.
R. sceleratus, L. 1, 2, 3, 5.
R. Flammula L. 1, 2, 4.
R. Lingua L. 1, 3, 4.
R. auricomus L. 1, 2, 3, 5.
R. acris L. 1, 2, 3, 4, 5, 6. The sub-species are not yet worked out for the county, but we seem to have (*c*) *Boræanus* and (*d*) *Steveni*.
R. repens L. 1, 2, 3, 4, 5, 6.
R. bulbosus L. 1, 2, 3, 5, 6.
R. sardous Crantz 1, 2, 3, 5. Very uncommon; in fact hardly ever seen.
R. parviflorus L. 1, 2, 3, 5. Not recently found.
R. arvensis L. 1, 2, 3, 5. Locally common.
R. Ficaria L. 1, 2, 3, 4, 5, 6.

Caltha palustris L. 1, 2, 3, 4, 5, 6.
(*b*) *Guerangerii* (Bor.) 1.
Helleborus viridis L.
(*b*) *occidentalis* (Reuter) 1, 2, 3. Doubtfully wild.
[*H. fœtidus*, L. 1, 3.]
[*Eranthis hyemalis* Salisb.]
Aquilegia vulgaris L. 1, 3, 4, 5.
[*Delphinium Ajacis* L. 1, 2, 3, 5.]

BERBERIDACEÆ.

[*Berberis vulgaris* L.]

NYMPHÆACEÆ.

Nymphæa lutea L. 1, 2, 3, 4, 5.
Castalia alba Wood 1, 3, 5.

PAPAVERACEÆ.

[*Papaver Somniferum* L.]
P. Rhœas L. 1, 2, 3, 4, 5, 6.
(*c*) *Pryorii* Druce 3.
P. dubium L. 1, 2, 3, 4, 5, 6.
P. Lecoqii Lamotte 1, 2, 3, 5. Now very seldom found in most parts; *P. dubium*, which was extremely rare thirty or forty years ago, seems to have supplanted it.
P. Argemone L. 1, 2, 3, 4, 5, 6.
P. hybridum L. 1, 3, 5. Much less common than formerly.
Roemeria hybrida. See former list.
Chelidonium majus L. 1, 2, 3, 4, 5, 6.

FUMARIACEÆ.

[*Corydalis lutea* DC.]
Fumaria Borœi Jord. 1.
F. Bastardi Bor. (= *confusa* Jord.) 1.
F. officinalis L. 1, 2, 3, 4, 5, 6.
F. densiflora DC. 3, 6.
F. parviflora Lam. 1. 3, 6.
F. Vaillantii Lois. 1, 3.

CRUCIFERÆ.

[*Cheiranthus Cheiri* L.]
Radicula Nasturtium-aquaticum Rendle & Britten 1, 2, 3, 4, 5, 6.
(*b*) *siifolia* (Rendle & Britten) 3.
R. sylvestris Druce 1, 3, 5.
R. palustris Mœnch. 1, 2, 3.
R. amphibia Druce 1, 3, 5.
Barbarea vulgaris Ait. 1, 2, 3, 6.
B. stricta Andrz. 3.
Arabis hirsuta Scop. 1, 3, 5, 6.

A. Turrita L. See former list.
Cardamine amara L. 1.
C. pratensis L. 1, 2, 3, 4, 5, 6.
(*b*) *dentata* (Schultes) 3 (Cherry Hinton: extinct).
C. hirsuta L. 1, 2, 4, 5.
[*Alyssum alyssoides* L.]
Erophila verna E. Meyer 1, 2, 3, 4, 6.
E. præcox DC. 1, 6.
E. virescens Jord. 4.
Cochlearia anglica L. 1. Apparently extinct near Wisbech, and not found nearer to the county than Denver.
[*C. Armoracia* L.]
Sisymbrium Thalianum Gay 1, 3, 4, 6.
S. officinale Scop. 1, 2, 3, 4, 5, 6.
(*b*) *leiocarpon* DC.
S. Sophia L. 1, 2, 3, 5, 6.
S. Irio. See former list.
S. Alliaria Scop. 1, 2, 3, 4, 5, 6.
Erysimum cheiranthoides L. 1, 2, 3, 5, 6.
[*E. orientale* Mill. 1, 3.]
[*Brassica campestris* L.
(*a*) *Napus* (L.).
(*b*) *Rutabaga* (DC.).
(*c*) *Rapa* (L.).]
B. nigra Koch 1, 2, 3, 5.
B. arvensis O. Kuntze 1, 2, 3, 4, 5, 6.
B. alba Boiss. 1, 2, 3, 5, 6.
[*B. Erucastrum* Vill. 3 (Devil's Dyke, near Newmarket).]
Diplotaxis muralis DC. 1, 2, 3.
(*b*) *Babingtonii* Syme 1, 2, 3.
D. muralis, and its biennial form *Babingtonii*, are thoroughly naturalized in districts 1, 2, 3, but not necessarily confined to them, especially on the railway lines.
Capsella Bursa-pastoris Medic. 1, 2, 3, 4, 5, 6.
Coronopus procumbens Gilib. 1, 2, 3, 4, 5.
Lepidium latifolium L. See former list.
L. ruderale L. 1, 3.
[*L. sativum* L.]
L. campestre Br. 1, 3, 5.
L. heterophyllum Benth.
(*b*) *Smithii* Hook. 1.
[*L. Draba* L. 1, 2, 3, 5.]
Thlaspi arvense L. 1, 2, 3. Babington gives no record later than that of Relhan, but we can now give Chatteris, Aldreth Bridge, Waterbeach, Bottisham Lode, Devil's Dyke, Six Mile Bottom and Abington Park.

Iberis amara L. 2, 3. Perhaps native in 3.

Teesdalia nudicaulis Br. 4. Still occurs in small quantity at Gamlingay, and may perhaps yet be found in 6 at or near Kennett, close to its Suffolk habitats.

[*Isatis tinctoria* L. 1. Cultivated for the Woad Mills at Parson's Drove, about six miles from Wisbech. The balls of manufactured woad are still used in combination with indigo to dye cloths for the Army and Navy. The mixture is said to give a more permanent colour than indigo alone.]

Raphanus Raphanistrum L. 1, 2, 3, 5, 6.

Resedaceæ.

Reseda lutea L. 1, 2, 3, 6.

R. Luteola L. 1, 2, 3, 4, 6.

Cistaceæ.

Helianthemum Chamæcistus Mill. 3, 4, 5, 6. A pale form occurs on the Hildersham Furze Hills, an orange form at Stetchworth.

Violaceæ.

Viola odorata L. 1, 3, 5, 6.

(*c*) *dumetorum* (Jord.) 1, 2, 3.

× *hirta* 1, 3.

V. hirta L. 1, 2, 3, 4, 5, 6.

(*b*) *Foudrasi* (Jord.) 3.

(*c*) *glabrata* Beeby.

(*d*) *pinetorum* Wiesb. 4.

V. calcarea Greg. 3.

V. sylvestris Kit. 1, 2, 3, 5.

(*c*) *punctata* Druce 2, 5.

V. Riviniana Reichb. 1, 3, 4, 5.

(*b*) *nemorosa* (N. W. & M.) 5.

V. ericetorum Hayne 1, 4.

(*b*) *crassifolia* (Grönv.) 1 (Chatteris Turf Fen, A. Fryer: first British record).

× *stagnina* 1.

× *Riviniana* 4.

V. stagnina Kit. 1. Still in Wicken Fen.

V. tricolor L. 1. The forms are not yet worked out for the county, but there is a large form near Haddenham.

(*b*) *arvensis* Murr. 1, 2, 3, 4, 5, 6.

Polygalaceæ.

Polygala vulgaris L. 1, 3, 4, 5.

P. serpyllacea Weihe 1. 4. Wimblington Firelots (Fryer), Chippenham Fen (Bennett), Gamlingay (Evans and Moss).

P. calcarea, F. Schultz. Recorded from Chippenham Moor by A. Fryer (*in litt.*), and allowed by A. Bennett.

Frankeniaceæ.

Frankenia lævis L. See former list.

Caryophyllaceæ.

Dianthus deltoides L. 3, 4. Found with pink and with white flowers at Hildersham; with pink at Gamlingay (1910).

[*D. Caryophyllus* L. 1, 6. Relhan records this species from Chippenham and Leverington.]

[*Saponaria officinalis* L. 1, 2, 3, 4, 6.]

Silene latifolia Rendle & Britten 1, 2, 3, 4, 5, 6.

(*b*) *puberula* (Jord.) 1, 2, 3, 5, 6.

S. conica L. 6.

S. Otites Wibel 6. In Babington's *Flora of Cambridgeshire* this species is erroneously entered as *S. anglica*, which grows in Suffolk near Chippenham, and may yet be found in the county.

S. noctiflora L. 1, 2, 3, 5, 6.

Lychnis alba Mill. 1, 2, 3, 4, 5, 6.

L. dioica L. 1. Found only as yet between Linton and Bartlow.

L. Flos-cuculi L. 1, 4, 5, 6.

L. Githago Scop. 1, 2?, 3, 5, 6.

Cerastium semidecandrum L. 1, 2, 3, 4, 6.

C. viscosum L. 1, 2, 3, 4, 5, 6.

C. vulgatum L. 1, 2, 3, 4, 5, 6.

C. arvense L. 1, 3, 4, 5, 6. Even on gault banks in 1.

Mœnchia erecta Gaertn. 4.

Stellaria aquatica Scop. 1, 2, 3, 5.

S. media Vill. 1, 2, 3, 4, 5, 6.

(*b*) *apetala* Ucria 1, 4, 6.

S. Holostea L. 1, 2, 3, 4, 5, 6.

S. palustris Retz. 1, 2, 3, 4.

S. graminea L. 1, 2, 3, 4, 6.

S. uliginosa Murr. 1, 4.

Arenaria tenuifolia L. 1, 2, 3, 6.

(*b*) *laxa* (Jord.) 1, 3.

A. trinervia L. 1, 4, 5.

A. serpyllifolia L. 1, 2, 3, 4, 5, 6.

A. leptoclados Guss. 1, 2, 3, 4, 5, 6.

Sagina maritima Don.

(*c*) *debilis* (Jord.) 1.

(*d*) *densa* (Jord.) 1 (Wisbech).

S. apetala Ard. 1, 2, 3, 4, 5, 6.
(*b*) *prostrata* Gibs. 1.
S. ciliata Fr. 1, 3, 4, 5, 6.
S. procumbens L. 1, 2, 3, 4, 5, 6.
S. nodosa Fenzl. 1, 3, 4, 6. A curious prostrate form of a dark green colour with opposite lateral branches, found at Wisbech, has not yet been determined.
Spergula arvensis L. 3, 4, 6.
S. sativa Bœnn. 4.
Spergularia rubra Pers. 1?, 3, 4.
S. salina Presl.
(*b*) *media* 1. River below Wisbech.
S. marginata Kittel 1. River below Wisbech.

PORTULACEÆ.

[*Claytonia perfoliata* Don 6. In great abundance at Kennett.]
Montia fontana L.
(*a*) *minor* All. 1, 2, 4.

HYPERICACEÆ.

Hypericum perforatum L. 2, 3, 4, 5, 6. *H. dubium* is said to occur near Kirtling (*J. of B.*, 1873, p. 274).
H. quadrangulum L. 1, 4, 5, 6.
H. humifusum L. 3, 4.
H. pulchrum L. 3, 4. Still found at Gamlingay, but Babington alone records the plant from Hinton.
H. hirsutum L. 3, 4, 5.
H. elodes L. See former list.

MALVACEÆ.

Althœa officinalis L. 1.
Malva moschata L. 1, 3, 5. Some of the records may refer to *heterophylla.*
(*b*) *heterophylla* Lej. 2.
M. sylvestris L. 1, 2, 3, 4, 5, 6.
M. rotundifolia L. 1, 2, 3, 5.

TILIACEÆ.

[*Tilia platyphyllos* Scop. Planted. Rare.]
[*T. vulgaris* Hayne. Planted.]
T. cordata Mill. 1, 4, 5.

LINACEÆ.

Radiola linoides Roth. 3. We have only Babington's record "near Newmarket."
Linum catharticum L. 1, 3, 4, 5, 6.

L. perenne L. 1, 3, 5.
[*L. usitatissimum* L.]

GERANIACEÆ.

Geranium sanguineum L. 3, 5. Records from Wood Ditton, Stetchworth and Balsham need confirmation, but the plant is still found on the Devil's Dyke not far from the two places first named.
[*G. phæum* L.]
G. pratense L. 1, 2, 3, 5.
G. pyrenaicum Burm. 1, 2, 3, 6. The pale-flowered form occurs on the Hills Road, the darker-flowered form elsewhere.
G. molle L. 1, 2, 3, 4, 5, 6.
G. pusillum L. 1, 2, 3, 4, 5, 6. Especially common in 6, and on fen banks.
G. rotundifolium 1, 3, 4. Only known at present in or near gardens at Chatteris and Newmarket; older records from Cambridge and Gamlingay will be found in Babington's *Flora of Cambridgeshire*.
G. dissectum L. 1, 2, 3, 4, 5, 6.
G. columbinum L. 3. Once found at Harlton (Babington's *Flora of Cambridgeshire*).
G. lucidum L. 1, 3. We have only the records in Babington's *Flora of Cambridgeshire*, from Wisbech, Quy, Chesterton and Barnwell.
G. Robertianum L. 1, 2, 3, 4, 5, 6.
Erodium cicutarium L'Her. 1, 3, 4, 5, 6 (on sandy or gravelly soil).
E. moschatum L'Her. 1, 4. In all probability a casual, but recently observed by A. H. Evans in Burwell Fen.

OXALIDACEÆ.

Oxalis Acetosella L. 5. Not recently observed. Babington's records probably all refer to 5.
[*O. stricta* L.]

BALSAMINEÆ.

[*Impatiens parviflora* DC.]

AQUIFOLIACEÆ.

Ilex Aquifolium L. Perhaps native in 4, 5, 6.

CELASTRACEÆ.

Euonymus europæus L. 1, 2, 3, 5, 6.

RHAMNACEÆ.

Rhamnus catharticus L. 1, 2, 3, 5, 6.
R. Frangula L. 1, 3, 4. Besides Wicken and Chippenham Fens, we have old records for Fulbourn, Wilbraham, Hildersham, Odsey, and Gamlingay.

ACERACEÆ.

[*Acer Pseudo-Platanus*, L. Planted.]
A. campestre L. 1, 2, 3, 4, 5, 6.
(*b*) *leiocarpon* Wallr. 5.

LEGUMINOSÆ.

Genista anglica L. 3, 4, 5.
G. tinctoria L. 3, 5.
3 refers to the Furze Hills, Hildersham, where sand overlies the chalk.
Ulex europœus L. 2, 3, 4, 5, 6. (Chiefly in 4, 6.)
U. minor Roth. 3. Probably extinct.
Cytisus scoparius Link. 1, 3, 4, 5, 6.
Ononis repens L. 1, 2, 3, 4, 5, 6.
(*b*) *horrida* Lange 3.
O. spinosa L. 1, 2, 3, 5, 6.
[*Medicago sativa* L.]
M. sylvestris Fr. 3, 6 (Hildersham, Snailwell, Chippenham).
M. Falcata L. 3, 6.
M. lupulina L. 1, 2, 3, 4, 5, 6.
M. arabica Huds. 1, 2, 4.
M. minima Desr. 3, 6.
Melilotus altissima Thuill. 1, 2, 3, 4, 5.
[*M. alba* Desr.]
[*M. officinalis* Lam. 1, 2, 3, 5, 6.]
[*M. indica* All. 2.]
Trifolium subterraneum L. 3, 4, 6?
T. pratense L. 1, 2, 3, 4, 5, 6.
(*c*) *parviflorum* (Bab.) 1.
T. medium L. 3, 5.
T. ochroleucon Huds. 1, 2, 3, 4, 5. Common in 5.
[*T. incarnatum* L.]
T. arvense, L. 1, 3, 4, 5, 6.
T. striatum L. 1, 2, 3, 4, 6. (On dry soil.)
T. scabrum L. 1, 2, 3, 4, 5, 6. (On sandy or gravelly soil.)
[*T. hybridum* L.]
T. repens, L. 1, 2, 3, 4, 5, 6.
T. fragiferum L. 1, 2, 3, 5.
T. procumbens L. 1, 2, 3, 4, 5, 6.
T. dubium Sibth. 1, 2, 3, 4, 5, 6.
T. filiforme L. 4. Records from near Cambridge and Ely need confirmation.
Anthyllis Vulneraria L. 1, 3, 6.
(*d*) *Allionii* DC. 1.
Lotus corniculatus L. 1, 2, 3, 4, 5, 6.
L. tenuis Waldst. & Kit. 2, 3, 4, 5.

L. uliginosus Schk. 1, 2, 3, 4, 5, 6. (With var. *glaber* Bréb. in 4.)
Astragalus danicus Retz 3, 5, 6.
A. glycyphyllos L. 1, 2, 3, 5.
Ornithopus perpusillus L. 4, 6.
Hippocrepis comosa L. 3, 6.
Onobrychis viciæfolia Scop. 1, 2, 3, 4, 5, 6.
Vicia hirsuta Gray 1, 2, 3, 4, 5.
V. tetrasperma Mœnch. 3, 4, 5.
V. gracilis Lois. 1, 2, 5.
V. cracca L. 1, 2, 3, 4, 5, 6.
V. sylvatica. See former list.
V. sepium L. 1, 2, 3, 5. (Very local.)
[*V. sativa* L.]
V. angustifolia L. 1, 6.
(*b*) *Bobartii* Koch 4.
V. lathyroides L. 5?, 6.
Lathyrus Aphaca L. 1, 2, 3, 5.
L. Nissolia L. 2. Near Long Stanton. Also recorded from near Ely by W. Cross (in litt. to A. Bennett) possibly from Haddenham, where Ray found the plant.
L. pratensis L. 1, 2, 3, 4, 5, 6.
L. sylvestris L. 3, 5.
L. palustris L. 1. There is also an old record by J. Martyn for Little Eversden.

Rosaceæ.

Prunus spinosa L. 1, 2, 3, 4, 5, 6.
(*b*) *macrocarpa* Wallr. 3, 5.
P. insititia L. 2, 3, 5, 6.
[*P. domestica* L.]
P. avium L. 3, 4.
P. Cerasus L. 3 (extinct).
[*P. Padus* L. Planted.]
Spiræa Ulmaria L. 1, 2, 3, 4, 5, 6.
S. Filipendula L. 1, 3, 4, 5, 6.
Rubus idæus L. 3, 4, 5.
(*b*) *obtusifolius* (Willd.) 5?
R. thyrsoideus Wimm. 1, 2?, 3, 5.
R. rusticanus Merc. 1, 2, 3, 4, 5, 6.
R. radula Weihe 5.
R. Koehleri Wh. & N. 3, 5.
R. dumetorum Wh. & N.
(*c*) *diversifolius* 3, 5.
R. corylifolius Sm.
(*a*) *sublustris* (Lees) 1, 2, 3, 5, 6.
R. Balfourianus Blox. 1, 3, 5.

R. cæsius 3, 5.
Geum urbanum L. 1, 2, 3, 4, 5, 6.
G. rivale L. 1, 5.
× *urbanum* (= *intermedium* Ehrh.) 5.
Fragaria vesca L. 1, 2, 3, 4, 5, 6.
Potentilla sterilis Garcke 1, 2, 3, 4, 5.
P. verna L. 3, 4. (4 refers to "White Wood, Gamlingay," Relhan.)
P. erecta Hampe 1, 2, 3, 4, 5, 6.
P. procumbens Sibth. 4, 5.
P. reptans L. 1, 2, 3, 4, 5, 6.
P. Anserina L. 1, 2, 3, 4, 5, 6.
P. argentea L. 1, 3, 4, 6. (1 refers to St Peter's College Grove, Cambridge.)
P. palustris Scop. 1, 4.
Alchemilla arvensis Scop. 1, 2, 3, 4, 5, 6.
A. vulgaris L. 3, 5. (Not found recently.)
Agrimonia Eupatoria L. 1, 2, 3, 4, 5, 6.
Poterium Sanguisorba L. 2, 3, 5, 6.
[*P. polygamum* Waldst. & Kit. 3, 5, 6.]
P. officinale A. Gray 1, 3, 5.

(The following list of Roses is only tentative and, it is hoped will soon be augmented.)

Rosa arvensis Huds. 1, 2, 3, 4, 5. (Chiefly in the west.)
R. stylosa Desv.
(*b*) *systyla* 1, 2, 3, 4, 5.
R. canina L. (agg.) 1, 2, 3, 4, 5.
(*o*) *surculosa* (Woods) 1, 3, 5.
R. micrantha Sm. 5, 6.
R. Eglanteria L. 3, 5, 6. (Other records doubtful.)
R. agrestis Savi.
(*d*) *inodora* Hook fil. 3, 5.
R. mollissima Willd. (= *tomentosa* Sm.) 3, 5.
var. *sherardi* (Davies).
R. villosa L. 1, 4. Recorded from near Cambridge and Gamlingay, and by Mr A. Fryer from near Chatteris. There are specimens, confirmed by Crépin, in Babington's Herbarium from Grantchester Lane and Balsham.
R. spinosissima L. 1. Recorded by Henslow only, from hedges in the fens near Swaffham Prior. Needs confirmation.
Pyrus torminalis Ehr. 5. (Little Gransden and Gamlingay Wood.)
P. Aucuparia Ehrh. 4, 5.
P. communis L. 3, 5.
P. Malus L.
(*a*) *acerba* (DC.) 1, 2, 3, 4, 5, 6.
(*b*) *mitis* (Wallr.) 5, 6.

Cratægus Oxyacantha L. 1, 2, 3, 4, 5, 6.
(*b*) *laciniata* Wallr.
(*c*) *kyrtostyla* (Fingerh.).
C. oxyacanthoides Thuill. 1, 2, 3, 4, 5, 6. Much less common than the last species; yet not rare.
× *Oxyacantha* 1, 2, 3.

SAXIFRAGACEÆ.

Saxifraga tridactylites L. 1, 2, 3, 4, 5, 6.
S. granulata L. 1, 2, 3, 5, 6.
Parnassia palustris L. 1, 3, 4.
[*Ribes Uva-crispa* L.]
[*R. nigrum* L.]
[*R. rubrum* L.]

CRASSULACEÆ.

Sedum Telephium L. 3, 5, 6.
[*S. album* L.
(*b*) *micranthum* Bast.]
[*S. dasyphyllum* L.]
S. acre L. 1, 2 ?, 3, 4, 5, 6. (Chiefly in 4, 6.)
[*S. sexangulare*, L.]
[*S. reflexum* L.]
[*Sempervivum tectorum* L.]

DROSERACEÆ.

Drosera rotundifolia L. 1, 3, 4. (Still in Chippenham Fen.)
D. anglica Huds. See former list.
D. longifolia L. See former list.

HALORAGACEÆ.

Hippuris vulgaris L. 1, 2, 3, 5.
Myriophyllum verticillatum L. 1, 2, 3, 4.
(*b*) *pectinatum* DC. 1 (W. West).
M. spicatum L. 1, 2, 3, 5.
M. alterniflorum DC. Gamlingay Brick Pits.
Callitriche stagnalis Scop. 1, 2, 3, 4, 5.
C. obtusangula Le Gall. 1, 2 (*C. palustris* L. and *C. intermedia* Hoffm. (= *hamulata* Kuetz) need confirmation).

LYTHRACEÆ.

Peplis Portula L. 4 (apparently extinct).
Lythrum Salicaria L. 1, 2, 6.
L. Hyssopifolia L. See former list.

ONAGRACEÆ.

Epilobium angustifolium L. 1, 4, 5.
E. hirsutum L. 1, 2, 3, 4, 5, 6.

E. parviflorum Schreb. 1, 2, 3, 5.
E. montanum L. 1, 2, 3, 4, 5, 6.
E. tetragonum Curt. 1, 2, 4, 5.
E. obscurum Schreb. 4. (See Babington's *Flora of Cambridgeshire.*)
E. palustre L. 1, 3, 4, 5.
[*Œnothera biennis*, L.]
Circœa lutetiana L. 1, 3, 4, 5.

CUCURBITACEÆ.

Bryonia dioica Jacq. 1, 2, 3, 4, 5, 6.

UMBELLIFERÆ.

Hydrocotyle vulgaris L. 1, 2, 3, 4.
Sanicula europœa L. 2, 3, 5.
Conium maculatum L. 1, 2, 3, 4, 5, 6.
Smyrnium Olusatrum L. 1, 2, 3.
Bupleurum rotundifolium L. 1, 3, 5.
B. tenuissimum L. 1, 3, 5. Hinton Moor (J. Martyn), Eltisley (Ray): near Wisbech, Sutton, Ely and Reach.
Apium graveolens L. 1, 2, 3, 5.
A. nodiflorum Reichb. fil. 1, 2, 3, 6.
(*e*) *repens* (Koch) 1, 3.
A. inundatum Reichb. fil. 1, 2, 3, 4.
Cicuta virosa L. See former list.
[*Carum Petroselinum* Benth. & Hook. fil.]
C. segetum Benth. & Hook. fil. 2, 3, 5.
[*C. Carvi* L. 1, 2, 3.]
C. Bulbocastanum Koch 3.
Sison Amomum L. 1, 2, 3, 4, 5.
Sium latifolium L. 1, 2.
S. erectum Huds. 1, 2, 4.
Ægopodium Podagraria L. 1, 2, 3, 4, 5, 6.
Pimpinella Saxifraga L. 2, 3, 4, 5, 6.
P. major Huds. 2, 5.
Conopodium majus Loret 2, 4, 5.
Chærophyllum temulum L. 1, 2, 3, 4, 5, 6.
Scandix Pecten-Veneris L. 1, 2, 3, 5, 6.
Anthriscus vulgaris Bernh. 1, 2, 3, 4, 6.
A. sylvestris Hoffm. 1, 2, 3, 4, 5, 6.
Seseli Libanotis Koch 3.
[*Fœniculum vulgare* Mill. 3, 5.]
Œnanthe fistulosa L. 1, 2, 4, 5.
Œ. silaifolia Bieb. 1. Extinct in Grantchester Fields, but still found on Sutton Washes.
Œ. Lachenalii C. Gmel. 1, 2, 3, 5.

Œ. aquatica Poir. 1, 2, 3, 5.
Œ. fluviatilis Colem. 1, 2, 3.
Æthusa Cynapium L. 1, 2, 3, 4, 5.
[*Siler trilobum* Crantz. (Cherry Hinton.)]
Silaus flavescens Bernh. 1, 2, 3, 5, 6.
Selinum Carvifolia L. 1.
Angelica sylvestris L. 1, 2, 3, 5, 6.
Peucedanum palustre Mœnch. 1.
P. sativum Benth. & Hook. fil. 1, 2, 3, 5, 6.
Heracleum Sphondylium L. 1, 2, 3, 4, 5, 6.
Daucus Carota L. 1, 2, 3, 4, 5, 6.
Caucalis latifolia L. See former list.
C. daucoides L. 1, 3, 5.
C. arvensis Huds. 1, 2, 3, 5, 6.
C. Anthriscus Huds. 1, 2, 3, 4, 5, 6.
C. nodosa Scop. 1, 2, 3, 5, 6.

Araliaceæ.

Hedera Helix L. 1, 2, 3, 4, 5, 6.

Cornaceæ.

Cornus sanguinea, L. 1, 2, 3, 5, 6.

Caprifoliaceæ.

Adoxa Moschatellina 1. Shelford (Relhan) and round Cambridge.
Sambucus nigra L. 1, 2, 3, 4, 5, 6.
[(*b*) *laciniata* Mill.]
S. Ebulus L. 1, 2, 3, 5.
Viburnum Opulus L. 1, 2, 3, 5, 6.
V. Lantana L. 1, 3, 5.
Lonicera Caprifolium L. 1, 2, 3, 6.
L. Periclymenum L. 1, 2, 3, 4, 5, 6.

Rubiaceæ.

Galium Cruciata Scop. 1, 2, 3, 4, 5, 6.
G. verum L. 1, 2, 3, 4, 5, 6.
× *erectum* 1 ? (Wicken Fen).
G. erectum Huds. 1, 2, 3, 4, 5.
G. Mollugo L. 1, 2, 3, 4, 5, 6.
G. saxatile L. 4, 6.
G. palustre L. 1, 2, 3, 4, 5, 6.
(*b*) *elongatum* (Presl.) 1, 2, 4, 5.
(*c*) *Witheringii* (Sm.) 1, 5.
G. uliginosum L. 1, 3, 4, 5, 6.
G. anglicum Huds. 1, 6.

G. Aparine L. 1, 2, 3, 4, 5, 6.
G. tricorne Stokes 1, 2, 3, 5.
Asperula odorata L. 3, 5. No record since 1860.
A. cynanchica L. 3, 5.
Sherardia arvensis L. 1, 2, 3, 4, 5, 6.

VALERIANACEÆ.

Valeriana dioica L. 1, 3, 5.
V. officinalis L. (= *Mikanii* Syme) 1, 3, 5.
V. sambucifolia Mikan. 1, 2, 3, 5.
[*Kentranthus ruber* DC.]
Valerianella olitoria Poll. 1, 2, 4.
V. rimosa Bast. 1, 5.
V. dentata Poll. 3, 5. Also found near Cottenham.

DIPSACACEÆ.

Dipsacus sylvestris Huds. 1, 2, 3, 5.
D. pilosus L. 1, 2, 3, 5.
Scabiosa Succisa L. 1, 2, 3, 4, 5, 6.
S. Columbaria L. 1, 3, 5, 6.
S. arvensis L. 1, 2, 3, 5, 6.

COMPOSITÆ.

Eupatorium cannabinum L. 1, 2, 3, 5, 6.
Solidago Virgaurea L. 4.
Bellis perennis L. 1, 2, 3, 4, 5, 6.
[*Aster salignus* 1 (Wicken Fen).]
A. Tripolium L. 1. (Extends inland as far as Sutton.)
[*Erigeron canadense* L. Thoroughly established and common in many places.]
E. acre L. 1, 3, 6. A record from Barton may refer to the gault (2).
Filago germanica L. 1, 2, 3, 4, 5, 6.
F. apiculata (G. E. Sm.) 4. Also in a garden at Chatteris.
F. spathulata (Presl.) 1, 2, 3, 4, 5, 6.
F. minima Fr. 1, 3, 4, 6.
Antennaria dioica Gaertn. 3, 4, 6 (not found recently).
Gnaphalium uliginosum L. 1, 2, 3, 4, 5.
(*b*) *pilulare* (Wahl.) has been found at King's Hedges near Cambridge, at Toft and near Chatteris.
G. luteo-album. See former list.
G. sylvaticum L. 4.
[*Inula Helenium* L. (not found recently).]
I. squarrosa Bernh. 1, 3, 6.
Pulicaria dysenterica Gray 1, 2, 3, 5, 6.
P. vulgaris Gaertn. See former list.

Bidens cernua L. 1, 3, 5.
B. tripartita L. 1, 2, 4, 5.
Achillæa Millefolium L. 1, 2, 3, 4, 5, 6.
A. Ptarmica L. 1, 2, 3, 4, 5. Rare in the county.
Anthemis Cotula L. 1, 2, 3, 5, 6.
A. arvensis L. 2, 3, 4, 5, 6. No recent record.
A. nobilis L. 1.
Chrysanthemum segetum L. 1, 2, 3, 4.
C. Leucanthemum L. 1, 2, 3, 5, 6.
[*C. Parthenium*, Bernh.]
Matricaria inodora L. 1, 2, 3, 4, 5, 6.
M. Chamomilla L. 1, 2, 3, 4, 5.
[*M. suaveolens* Buch. 1. (Foul Anchor.)]
Tanacetum vulgare L. 1, 2, 3, 4, 5.
Artemisia Absinthium L. 1, 2, 3, 4.
A. vulgaris L. 1, 2, 3, 4, 5, 6.
A. maritima L. 1.
Tussilago Farfara L. 1, 2, 3, 4, 5, 6.
[*Petasites fragrans* Presl.]
P. ovatus Hill 1, 3, 5, 6.
Senecio vulgaris L. 1, 2, 3, 4, 5, 6.
× *squalidus*. A weed in the Botanic Garden, introduced from Oxford.
S. sylvaticus L. 1, 2, 3, 4.
S. viscosus L. 1, 2?, 4? (Recently found on waste ground at Cambridge.)
S. erucifolius L. 1, 2, 3, 4, 5.
S. Jacobæa L. 1, 2, 3, 4, 5, 6. (Has increased much during the last thirty years on fields that were once wet fen.)
S. aquaticus Hill 1, 2, 3, 4, 5, 6.
S. paludosus L. See former list.
S. palustris Hook. See former list.
S. integrifolius Clairv. 3.
Carlina vulgaris L. 1, 2, 3, 5.
Arctium majus Bernh. 1, 2, 3, 5, 6.
(*b*) *subtomentosum* Lange 1, 2, 5.
A. nemorosum Lej. 1, 2, 3, 5.
A. minus Bernh. 1, 2, 3, 5, 6.
A. pubens Bab. (= *intermedium* Lange *fide* Bab. in Herb.) 1, 2, 3, 5, 6.
Carduus nutans L. 1, 2, 3, 5, 6.
C. crispus L. 1, 2, 3, 5, 6.
Cnicus lanceolatus Willd. 1, 2, 3, 4, 5, 6.
C. eriophorus Roth. 2, 3, 5. (Also as a casual at Cambridge.)
C. palustris Willd. 1, 2, 3, 4, 5, 6.
C. pratensis Willd. 1, 3.

C. acaulis Willd. 1, 2, 3, 4, 5, 6.
(*b*) *caulescens* Pers. 3.
C. arvensis Hoffm. 1, 2, 3, 4, 5, 6.
[*Onopordum Acanthium* L. 1, 2, 3, 4, 5, 6.]
[*Silybum Marianum* Gaertn. 1, 2, 3.]
Serratula tinctoria L. 1, 2, 3, 5.
Centaurea nigra L. 1, 2, 3, 4, 5, 6.
C. Scabiosa L. 1, 2? 3, 4, 5, 6.
C. Cyanus L. 1, 2, 3, 4, 5, 6. (Now very rare.)
C. Calcitrapa L. 1, 3. Not recorded since Babington wrote in 1860.
[*C. solstitialis* L. 1, 2, 3. Still occurs near Hildersham, Dullingham and Doddington.]
Cichorium Intybus L. 1, 2, 3, 5, 6.
Arnoseris minima Schweigg. & Koerte. See former list.
Lapsana communis L. 1, 2, 3, 4, 5, 6.
Picris hieracioides L. 1, 3, 4, 5.
P. echioides L. 1, 2, 3, 5.
Crepis fœtida L. See former list.
C. taraxacifolia Thuill. 1, 2, 3, 5.
C. capillaris Wallr. 1, 2, 3, 4, 5, 6.
C. biennis L. 2, 3.
Hieracium Pilosella L. 1, 3, 4, 5, 6.
H. boreale (Fr.) 4.
H. umbellatum L. 3, 4. Recorded from Hildersham by J. Martyn and from Gamlingay by P. Dent.
Hypochœris glabra L. 4, 6.
H. radicata L. 1, 2, 3, 4, 5, 6.
H. maculata L. 3.
Leontodon nudicaule Banks & Soland L. 1, 3, 4, 5, 6.
L. hispidum L. 1, 2, 3, 5, 6.
L. autumnale L. 1, 2, 3, 4, 5, 6.
Taraxacum officinale Weber. Common.
T. erythrospermum Andrz. 1, 3, 4, 6.
T. palustre DC. 1. The true plant is common in parts of the Fens, and is said to have occurred elsewhere.
(*b*) *udum* (Jord.) 1.
Lactuca virosa L. 1, 3. (Not observed since 1860.)
L. Serriola L. 1, 2, 3. This species was probably always an alien: it was last seen about 1885 by Mr A. Fryer, at Chatteris.
L. saligna L. 1. (Still found near Mepal.)
L. muralis Gaertn. 1, 6.
Sonchus oleraceus L. 1, 2, 3, 4, 5, 6.
S. asper Hill 1, 2, 3, 4, 5, 6.
S. arvensis L. 1, 2, 3, 4, 5, 6.
S. palustris L. See former list.

Tragopogon pratense L.
(*b*) *minus* (Mill.) 1, 2, 3, 4, 5, 6.
[*T. porrifolius* L.]
× *pratense* 1. (Found at Chesterton by Mr A. Wallis.)

Campanulaceæ.

Jasione montana L. 3, 4. (Newmarket, Hildersham and still at Gamlingay.)
Campanula glomerata L. 3, 5.
C. Trachelium L. 3, 5.
C. latifolia L. 2?, 5. (Comberton, Wood Ditton, Cheveley, Ely, not confirmed as a native.)
[*C. rapunculoides* L.]
C. rotundifolia L. 1, 3, 4, 5, 6.
Legousia hybrida Delarbre. 1, 2, 3, 5, 6.

Vacciniaceæ.

Oxycoccos quadripetala Gilib. See former list.

Ericaceæ.

Calluna vulgaris Hull. 3, 4, 6. Local.
Erica Tetralix L. 4.
E. cinerea L. See former list.

Monotropaceæ.

Monotropa Hypopitys L. 3, 5.

Plumbaginaceæ.

Limonium vulgare Mill. 1.
L. reticulatum Mill. See former list.
Statice maritima Mill. 1.

Primulaceæ.

Hottonia palustris L. 1, 2, 3. (Almost confined to 1.)
Primula elatior Jacq. 5.
× *veris* 5. Rare.
× *vulgaris* 5. Locally abundant.
P. vulgaris Huds. 1, 3, 5.
(*b*) *caulescens* Koch 5.
P. veris L. 1, 3, 5, 6.
× *vulgaris* 5. Rare.
Lysimachia vulgaris L. 1, 2, 3, 5.
L. Nummularia L. 1, 2, 3, 5.
L. nemorum L. See former list.
Glaux maritima L. 1.

Anagallis arvensis L. 1, 2, 3, 4, 5, 6. (With blue flowers in 1.)
A. fœmina Mill. 1, 2, 3. Some of the records may refer to blue-flowered *A. arvensis.*
A. tenella Murr. 1, 3, 4.
Centunculus minimus L. 4. (Not recorded since 1860.)
Samolus Valerandi L. 1, 2, 3, 4, 5, 6.

OLEACEÆ.

Fraxinus excelsior L. 1, 2, 3, 4, 5, 6.
Ligustrum vulgare L. 1, 2, 3, 4, 5, 6. Often planted.

APOCYNACEÆ.

[*Vinca major* L.]
[*V. minor* L. 1, 3, 5.]

GENTIANACEÆ.

Blackstonia perfoliata Huds. 1, 2, 3, 5.
Centaurium umbellatum Gilib. 1, 2, 3, 4, 5, 6.
C. pulchellum Druce 1, 2, 3, 5, 6.
Gentiana Amarella L. 1, 3, 5.
(*b*) *axillaris* Murb. 1, 5.
Menyanthes trifoliata L. 1, 3, 4.
Nymphoides peltatum Rendle & Britten 1, 2. (Locally abundant.)

BORAGINACEÆ.

Cynoglossum officinale L. 1, 2, 3, 5, 6.
[*Asperugo procumbens* L. Recorded by Ray from Newmarket.]
Symphytum officinale L. 1, 2, 3, 5.
(*b*) *patens* (Sibth.) Wisbech (Skrimshire).
[*Borago officinalis* L.]
[*Anchusa sempervirens* L.]
Lycopsis arvensis L. 1, 2, 3, 4, 6.
Myosotis cespitosa Schultz 1, 2, 4, 5.
M. palustris Hill 1, 3, 4, 6.
(*b*) *strigulosa* (Reichb.) 1.
M. arvensis Hill 1, 2, 3, 5, 6.
(*b*) *umbrosa* (Bab.) 1, 5.
M. collina Hoffm. 1, 3, 4, 6.
M. versicolor Sm. 1, 3, 4.
Lithospermun officinale L. 1, 2, 3, 5, 6.
L. arvense L. 1, 3, 5, 6.
Echium vulgare L. 1, 3, 5, 6.

CONVOLVULACEÆ.

Calystegia sepium Br. 1, 2, 3, 4, 5, 6. Well established in Wicken Fen and elsewhere.
Convolvulus arvensis L. 1, 2, 3, 4, 5, 6.

Cuscuta europæa L. 1, 2, 3, 5.
C. Epithymum Murr. 4.
C. Trifolii Bab.? (West, *J. of Bot.* 1898, p. 254.)

SOLANACEÆ.

Solanum Dulcamara L. 1, 2, 3, 4, 5, 6.
S. nigrum L. 1, 2, 3, 4, 5, 6.
[*Lycium chinense* Mill.]
Atropa Belladonna L. 1, 2, 3, 5.
[*Datura Stramonium* L.]
Hyoscyamus niger L. 1, 2, 3, 5, 6 (of uncertain appearance).

SCROPHULARIACEÆ.

Verbascum Thapsus L. 1, 2, 3, 4, 5, 6.
V. nigrum L. 3, 5, 6.
[*Linaria Cymbalaria* Mill. 1, 2, 3, 4, 5, 6.]
L. Elatine Mill. 1, 2, 3, 5, 6.
L. spuria Mill. 1, 2, 3, 5, 6.
[*L. purpurea* Mill.]
L. vulgaris Mill. 1, 2, 3, 4, 5, 6.
L. minor Desf. 2, 3, 4, 5, 6.
[*Antirrhinum majus* L.]
A. Orontium L. 3, 6.
Scrophularia aquatica L. 1, 2, 3, 4, 5, 6.
S. nodosa L. 1, 2, 3, 4, 5.
[*S. vernalis* L.]
Limosella aquatica L. 1, 4.
Digitalis purpurea L. 4, 5. First found by Mr R. H. Adamson and Dr C. E. Moss in 1909 in White Wood, Gamlingay. It also occurs in Gamlingay wood.
Veronica hederæfolia L. 1, 2, 3, 4, 5, 6.
V. didyma Ten. (=*polita* Fr.) 1, 2, 3, 4, 5, 6.
(*b*) *grandiflora* (Bab.) 3, 5?
V. agrestis L. 1, 2, 3, 4, 5, 6.
V. Tournefortii C. Gmel. 1, 2, 3, 4, 5, 6.
V. arvensis L. 1, 2, 3, 4, 5, 6.
V. serpyllifolia L. 1, 2, 5.
V. spicata L. See former list.
V. officinalis L. 3, 4, 5, 6.
V. Chamædrys L. 1, 2, 3, 4, 5, 6.
V. montana L. 2, 3, 4, 5. (Observed in Doddington Wood by A. Fryer (1881).)
V. scutellata L. 1, 2, 3, 4, 5, 6. (Decidedly rare, though widely spread.)
V. Anagallis L. 1, 2.
V. Beccabunga L. 1, 2, 3, 4.

Euphrasia Kerneri Wettst. 3.
E. borealis (Towns.) 1.
E. stricta (Host.) 3.
E. nemorosa H. Mart. 5.
Bartsia Odontites Huds. 1, 2, 3, 4, 5, 6.
Pedicularis palustris L. 1, 3, 4.
P. sylvatica L. 3, 4, 5. Last found at Chippenham (A. Fryer, 1883, in litt.).
Rhinanthus Crista-galli L. 1, 3, 5.
R. stenophyllus Schur. 1.
Melampyrum cristatum L. 4, 5.
M. pratense L. 4, 5. (Not observed of recent years.)

Orobanchaceæ.

Orobanche major L. 1, 4.
O. elatior Sutton 1, 3, 5. (*O. hederæ* and *O. rubra* are grown in the Botanic Garden at Cambridge from seed.)
O. Picridis F. Schultz 5.
O. minor Sm. 1, 3, 5, 6.
Lathræa Squamaria L.

Lentibulariaceæ.

Utricularia vulgaris L. 1, 2, 3. (*U. major* is suspected by Mr A. Bennett to occur in Burwell Fen. See *J. B.* 1903, p. 245.)
U. minor L. 1, 2, 3, 4. (Now confined to 1.)
Pinguicula vulgaris L. 1, 3, 4.

Verbenaceæ.

Verbena officinalis L. 1, 2, 3, 5, 6.

Labiatæ.

[*Mentha rotundifolia* Huds. 1 ?, 3. Reported only by Dent and Relhan.]
[*M. longifolia* Huds. 1, 2, 3. The records are somewhat doubtful.]
[*M. spicata* L.]
M. piperita L. 1, 2, 3, 5.
M. aquatica L. 1, 2, 4, 5.
× *arvensis* (*sativa* L.) 1, 3, 5, 6.
(*b*) *paludosa* Sole 1, 5.
M. gentilis L. 1.
M. arvensis L. 1, 2, 3, 4, 5, 6.
M. Pulegium L. 1, 3. (Not observed recently.)
Lycopus europæus L. 1, 2, 3, 4.
Origanum vulgare L. 1, 3.
Thymus Serpyllum L. 3, 5.
T. præcox Opiz 1.

T. Chamædrys Fr. 1, 3, 4, 6. *T. lanuginosus* Schk has been recorded from the Gog-Magog Hills (*J. of B.* 1908, p. 313); but see *Watson Botanical Exchange Club*, 1909—1910, p. 251.
Clinopodium vulgare L. 1, 3, 4, 5, 6.
Calamintha Acinos Clairv. 1, 3, 5, 6.
C. Nepeta Savi. 1, 3, 6.
C. montana Lam. 1, 3, 5, 6.
Salvia Verbenaca L. 1, 3, 5, 6.
Nepeta Cataria L. 1, 2?, 3, 5, 6.
N. hederacea Trev. 1, 2, 3, 4, 5, 6.
Scutellaria galericulata L. 1, 2, 3, 4.
Prunella vulgaris L. 1, 2, 3, 4, 5, 6.
P. laciniata L. 1. Recently found near Cambridge by Mr G. Goode.
Marrubium vulgare L. 1, 2, 3, 4.
Stachys officinalis Trev. (= *Betonica* Benth.) 1, 3, 4, 5.
S. palustris L. 1, 2, 3, 4, 5.
× *sylvatica* (= *ambigua* Sm.) Fen Ditton (Relhan), Coton (Newbould).
S. sylvatica L. 1, 2, 3, 4, 5, 6.
S. arvensis L. 1, 3, 5.
Galeopsis angustifolia Ehrh. 1, 3, 5, 6.
G. speciosa Mill. 1, 2, 3.
G. Tetrahit L. 1, 2, 3, 4, 5, 6.
[*Leonurus Cardiaca* L. 1, 3.]
Lamium amplexicaule L. 1, 2, 3, 4, 5, 6.
L. hybridum Vill. 1, 2, 3.
L. purpureum L. 1, 2, 3, 4, 5, 6.
[*L. maculatum* L.]
L. album L. 1, 2, 3, 4, 5, 6.
L. Galeobdolon Crantz 3, 5.
Ballota nigra L. 1, 2, 3, 4, 5, 6.
Teucrium Scordium L. See former list.
T. Scorodonia L. 4. (Henslow also gives Ely.)
Ajuga reptans L. 1, 2, 3, 5.
A. Chamæpitys Schreb. 3.

Plantaginaceæ.

Plantago major L. 1, 2, 3, 4, 5, 6.
P. media L. 1, 2, 3, 4, 5, 6.
P. lanceolata L. 1, 2, 3, 4, 5, 6.
[(*b*) *Timbali* (Jord.)]
P. maritima L. 1.
P. Coronopus L. 1, 4.
Littorella uniflora Aschers. 3, 4 (Ray and Relhan only).

Illecebraceæ.

Herniaria glabra L. 3. Found in 1855 by Newbould near Six Mile Bottom. It grows near our borders in Suffolk.
Scleranthus annuus L. 1, 3, 4, 6.

Amaranthaceæ.

[*Amaranthus Blitum* L.]

Chenopodiaceæ.

Chenopodium polyspermum L. 1, 2, 4, 5.
(*b*) *cymosum* Moq. 1.
C. Vulvaria L. 1.
C. album L. 1, 2, 3, 4, 5, 6.
(*b*) *viride* (Syme) 1, 4.
(*c*) *paganum* (Reichb.).
C. serotinum L. 1, 2, 3, 4.
C. murale L. 1. (Disappears and reappears—Waterbeach, 1906, A. H. Evans.)
C. hybridum L. 1, 2.
C. urbicum L. See former list.
C. rubrum L. 1, 2, 3.
C. Bonus-Henricus L. 1, 2, 3, 4, 5.
Beta maritima L. 1.
Atriplex littoralis L. See former list.
A. patula L. Common.
(*b*) *erecta* (Huds.) 1, 2, 3, 5.
(*c*) *angustifolia* (Sm.) 1, 2, 3, 5.
A. hastata L. Common.
A. deltoidea Bab. 1, 2, 3, 5.
A. Babingtonii Woods 1.
A portulacoides L. 1.
A. pedunculata L. See former list.
Salicornia europæa L. (= *stricta* Dum.) 1.
Suæda maritima Dum. 1.
(*b*) *procumbens* Syme 1.

Polygonaceæ.

Polygonum Convolvulus L. Common.
(*b*) *subalatum* V. Hall 2, 4.
P. aviculare L. Common. The forms of this species need further working out before the distribution can be properly given for the county.
P. Hydropiper L. 1, 4, 5.
P. minus Huds. 1. Now only known from the Old Bedford River.
P. mite Schrank 1.

P. Persicaria L. Common.
P. lapathifolium L. Common.
P. maculatum Trim. & Dyer 1.
P. amphibium L. 1, 2, 3, 4, 5.
P. Bistorta L. 1, 2, 3. Not seen recently.
[*Fagopyrum sagittatum* Gilib. A common crop with Fen farmers.]
Rumex conglomeratus Murr. 1, 2, 3, 5.
R. sanguineus L. We have only Newbould's doubtful records from Eversden and Kingston Woods.
(*b*) *viridis* (Sibth.) 1, 2, 3, 4, 5, 6.
R. maritimus L. 1, 2, 5.
R. limosus Thuill. 1.
R. pulcher L. 1, 2, 3, 4, 5, 6.
R. obtusifolius L. 1, 2, 3, 4, 5, 6.
R. crispus L. 1, 2, 3, 4, 5, 6.
× *obtusifolius* 1, 2.
R. Hydrolapathum Huds. 1, 2, 3.
R. Acetosa L. 1, 2, 3, 4, 5, 6.
R. Acetosella L. 1, 2, 3, 4, 5, 6.

Thymeleaceæ.

Daphne Laureola L. 1, 2, 3, 5 (mainly on boulder clay).

Loranthaceæ.

Viscum album L. Cambridge, doubtless introduced; Borley Wood on the oak (W. West).

Santalaceæ.

Thesium humifusum DC. 3. As a locality, Chippenham Park Avenue (A. H. Evans) is interesting, as it confirms Relhan's locality "Chippenham."

Euphorbiaceæ.

Euphorbia Helioscopia L. 1, 2, 3, 4, 5.
E. platyphyllos L. 2, 5.
E. amygdaloides L. 5.
E. Peplus L. 1, 2, 3, 4, 5, 6.
E. exigua L. 1, 2, 3, 4, 5, 6.
Mercurialis perennis L. 1, 2, 3, 4?, 5.
M. annua L. 4, 6. (On greensand at Ely; at Fordham and Chippenham.)

Urticaceæ.

Ulmus glabra Huds. *nec* Mill (= *montana* Stokes). Rare in all the districts.

U. procera Salisb. (= *glabra* Mill *nec* Huds.). Common and widely spread.

× *glabra* (= Huntingdon Elm). Commonly planted.

U. campestris L. (= English Elm). Round most towns and villages. Local in hedgerows.

U. hollandica Mill (= *major* Sm.). Local, in hedgerows.

U. sativa Mill. Rather common.

Humulus Lupulus L. 1, 2, 3, 4, 5, 6.

Urtica dioica L. Common.

(*b*) *angustifolia* Wimm. & Gräb.

[*U. pilulifera* L.

(*b*) *Dodartii* (L.). See former list.]

U. urens L. 1, 4, 6.

Parietaria ramiflora Mœnch. 1, 2, 3, 5, 6.

Myricaceæ.

Myrica Gale L. See former list.

Cupuliferæ.

Betula alba L. Frequently planted.

B. pubescens Ehrh. 1, 2, 4, 5, 6. Perhaps native in the Fens and on Gamlingay greensand.

(*b*) *denudata* E. S. Marshall 1, 4, 6.

Alnus glutinosa Gaertn. 1, 3, 4, 5, 6.

Carpinus Betulus L. 1, 2, 3, 4, 5.

Corylus Avellana L. 1, 2, 3, 4, 5.

[*Quercus Cerris* 4. Introduced. At Gamlingay it springs up on the greensand from self-sown seed.]

Q. sessiliflora (Salisb.) 4. First record 1908, from White Wood, Gamlingay, by C. E. Moss.

Q. Robur L. Common.

× *sessiliflora* 4. First record 1908, from White Wood, Gamlingay, by C. E. Moss.

[*Castanea sativa* Mill. Self-sown on the Gamlingay greensand.]

Fagus sylvatica L. Perhaps native on the Gamlingay greensand and on the chalk.

Salicaceæ.

Salix triandra L. 1, 2, 3, 4.

(*b*) *Hoffmaniana* (Sm.) 1, 4, 6.

S. fragilis L. 1, 2, 4.

S. alba L. 1, 2, 3, 4, 5, 6.

(*c*) *vitellina* (L.) 1.

× *fragilis* (= *viridis* Fr.).

× *triandra* (= *undulata* Ehrh.). Relhan records this form from Chesterton and Aldreth.

S. purpurea L. 1, 6.
var. *Forbyana* (Sm.) 1, 5.
× *viminalis* (= *rubra* Huds.) 1, 3.
S. viminalis L. 1, 2, 3, 5.
× *acuminata* 1, 3.
S. Caprea L. 1, 2, 3, 4, 5, 6.
S. aurita L. 1, 3, 4, 5, 6. The records need confirmation.
S. cinerea L. 1, 2, 5, 6.
var. *aquatica* (Sm.) 2, 3, 5.
var. *oleifolia* (Sm.) 1, 5.
S. repens L. 1, 3, 4.
[*Populus alba* L. Planted.]
P. canescens Sm. 1, 3, 4, 6.
P. tremula L. 1, 2, 3, 4, 5. Perhaps native at Gamlingay.
(*b*) *villosa* (Lange) 5.
P. nigra L. 1, 2, 3, 6. Rare.
[*P. canadensis* Mœnch. Very common, but always planted.]

Ceratophyllaceæ.

Ceratophyllum demersum L. 1, 2, 3, 5.
C. submersum L. 1.

Monocotyledones.

Hydrocharideæ.

[*Elodea canadensis* Michx. 1, 2, 3, 5.]
Hydrocharis Morsus-ranæ L. 1.
Stratiotes Aloides L. 1, 2.

Orchidaceæ.

Malaxis paludosa Sw. See former list.
Liparis Loeselii Rich. See former list.
Neottia Nidus-avis Rich. 5.
Listera ovata Br. 1, 3, 5, 6.
Spiranthes spiralis Koch 1, 3.
Cephalanthera grandiflora Gray 3. Locally plentiful.
Helleborine latifolia Druce 5?
H. media E. S. Marshall 3, 5.
H. longifolia Rendle & Britten (= *Epipactis palustris* Crantz) 1, 3, 4. Extinct at Gamlingay.
Orchis pyramidalis L. 1, 3, 5.
O. ustulata L. 3.
O. morio L. 1, 2, 3, 5.
O. mascula L. 1, 3, 5.
O. incarnata L. 1, 3.

O. latifolia L. 1, 3, 5.
O. maculata L. 1, 2, 3, 4, 5.
Aceras anthropophora Br. 3.
Ophrys apifera Huds. 1, 2, 3, 5.
O. sphegodes. See former list.
O. muscifera Huds. 1, 3, 5.
Herminium Monorchis Br. 3.
Habenaria conopsea Benth. 1, 2, 3, 5.
H. viridis Br. 1, 3, 5.
H. bifolia Br. 3.
H. virescens Druce (= *chloroleuca* Ridley) 2, 3, 5.

Iridaceæ.

Iris fœtidissima L. 1, 3, 5.
I. Pseudacorus L. 1, 2, 3, 5, 6.

Amaryllidaceæ.

Narcissus Pseudo-Narcissus L. 1, 3. Doubtfully native.

Dioscoreaceæ.

Tamus communis L. 1, 2, 3, 5.

Liliaceæ.

Ruscus aculeatus L. 2, 3.
Convallaria majalis L. 4. Native in a wood at Gamlingay.
Allium vineale L. 1, 2, 3, 5, 6.
A. oleraceum L. 3.
A. ursinum L. 1, 5.
Muscari racemosum Lam. & DC. 3.
Scilla non-scripta Hoffmgg. & Link 2, 3, 4, 5.
[*Ornithogalum nutans* L. 1, 3.]
O. umbellatum L. 6.
O. pyrenaicum L. Recorded by Dent from Eversden.
Fritillaria Meleagris L. See former list.
Colchicum autumnale L. See former list.
Narthecium ossifragum Huds. See former list.
Paris quadrifolia L. 5.

Juncaceæ.

Juncus bufonius L. 1, 2, 4, 5, 6.
J. squarrosus L. 4. Formerly in 3 also.
J. compressus L. 1, 2. Formerly in 3 also.
J. Gerardi Lois. 1.
J. inflexus L. (= *glaucus* Ehrh.) 1, 2, 3, 4, 5, 6.
J. effusus L. 1, 2, 4, 5.

J. conglomeratus L. 1, 2, 4, 5. Some of the records need confirmation.
J. bulbosus L. (= *supinus* Mœnch.) 1, 3, 4, 5.
J. subnodulosus Schrank (= *obtusiflorus* Ehrh.) 1, 3.
J. articulatus L. 1, 2, 3, 4, 5, 6.
J. sylvaticus Reich. (= *acutiflorus* Ehrh.) 1, 2, 4, 5.
Luzula pilosa Willd. 5.
L. sylvatica Gaud. is recorded from Wood Ditton in Babington's *Flora of Cambridgeshire, q.v.*
L. campestris DC. 1, 3, 4, 5, 6.
L. multiflora DC. 1, 3, 4, 6.
(*b*) *congesta* (Lej.) 1, 4, 6.

Typhaceæ.

Typha latifolia L. 1, 2, 3, 4, 5.
T. angustifolia L. 1, 2, 3, 5, 6.
Sparganium erectum L. (= *ramosum* Curt.). Common.
S. simplex Huds. 1, 2, 5.
S. minimum Fr. 1, 3. 3 refers to Triplow Peat Holes.

Araceæ.

Arum maculatum L. 1, 2, 3, 4, 5, 6.
Acorus Calamus L. 1, 2. (Lately found at Roswell Pits by A. H. Evans.)

Lemnaceæ.

Lemna trisulca L. 1, 2, 3, 5.
L. minor L. Common.
L. gibba L. 1, 2, 3, 5.
L. polyrrhiza L. 1, 2, 5.

Alismaceæ.

Alisma Plantago-aquatica L. 1, 2, 4, 5.
var. *graminifolium* Wahl. 1.
A. ranunculoides L. 1, 2, 3.
Sagittaria sagittifolia L. 1, 2, 3, 5.
var. *Bollei* 1.
Butomus umbellatus L. 1, 2, 5.

Naiadaceæ*.

Triglochin palustre L. 1, 4.
T. maritimum L. 1. See former list.
Potamogeton natans L. 1, 3, 4, 5, 6.
× *lucens* (= *fluitans* Roth.) 1. Near Chatteris.
× *coriaceus* (= × *crassifolius* Fryer) 1. Near Chatteris.
P. polygonifolius Pourr. 1, 4. Burwell Fen (Relhan), Bottisham

* The genus *Potamogeton* has been revised for us by Mr A. Fryer.

Fen (Dalton), Gamlingay. Specimens from all these places allowed by A. Bennett.

P. coloratus Hornem. 1, 3.

× *coriaceus* (= × *Billupsii* Fryer) 1. Benwick and Burwell.

P. heterophyllus Schreb. 1, 4. (Extinct at Gamlingay?)

× *Zizii* (= × *varians* Morong) 1. Near Chatteris.

× *pusillus* (= *lanceolatus* Sm.) 1. (Burwell Fen. A. Bennett.)

× *perfoliatus* (= × *nitens* Weber) 1. Near Chatteris.

P. graminifolius (Fr.) 1. Near Chatteris.

P. Zizii Koch (= *angustifolius* Bercht. & Presl.) 1.

P. lucens L. 1.

× *perfoliatus* (= *decipiens* Nolte) 1, 3.

× *heterophyllus*? (= *coriaceus* Fryer) 1.

P. prælongus Wulf. 1.

P. perfoliatus L. 1, 2.

× *coriaceus* (= *involutus* Fryer) 1. Black Bush Drove, Whittlesey.

P. crispus L. 1, 2, 3, 4, 5, 6.

× *perfoliatus* (= *Cooperi* Fryer) 1. Benwick.

P. densus L. 1.

P. zosterifolius Schum. 1, 2. Cambridge, Baitsbite, Ely (Babington), Roswell Pits, Bottisham Fen.

P. Friesii Rupr. 1, 2, 3.

P. pusillus, L. 1, 3, 4.

P. trichoides Cham. 1. Mepal (Fryer).

P. pectinatus L. 1.

P. flabellatus Bab. 1.

(*b*) *scoparius* Fryer 1.

Ruppia rostellata Koch 1. Babington refers a record of Skrimshire's from below Wisbech to this species, with some doubt.

Zannichellia palustris L. 1.

(*c*) *repens* Boenn. 1, 2.

Zostera marina L.

(*c*) *angustifolia* Hornem. 1. Below Wisbech.

Cyperaceæ.

Eleocharis acicularis Roem. & Schult. 1, 2.

E. palustris Roem. & Schult. 1, 2.

E. multicaulis Sm. 1, 4.

Scirpus pauciflorus Lightf. 1, 3, 4.

S. cæspitosus L. 1.

S. fluitans L. 1, 4.

S. setaceus L. 1, 4.

S. lacustris L. 1, 2, 3, 5.

S. Tabernæmontani Gmel. 1, 5.

S. maritimus L. 1. Occurs as far inland as Sutton and Upware.

S. compressus Pers. 1, 3. Not seen since about 1880.
Eriophorum angustifolium Roth. 1, 3, 4.
E. latifolium Hoppe 1, 3. Needs confirmation.
Rynchospora alba Vahl. 4. See former list.
Schœnus nigricans, L. 1, 3, 4. Not now at Gamlingay?
Cladium Mariscus Br. 1, 3.
Carex dioica L. 3, 4 (extinct).
C. pulicaris L. 1, 3.
C. disticha Huds. 1, 2, 3.
C. arenaria L. 6?
C. diandra Schrank 1, 3. Not found recently.
C. paradoxa Willd. 1. Discovered in Wicken Fen by Mr A. Fryer.
C. paniculata, L. 1, 3, 4.
C. vulpina, L. 1, 2, 4, 5.
var. *nemorosa*, 5.
C. muricata L. 1, 2, 3, 4, 5, 6.
C. divulsa Stokes, 1, 2, 3, 4, 5, 6.
C. echinata Murr. 1, 3, 4, 5. Found lately only at Gamlingay and Chippenham Fen.
C. remota L. 2, 3, 5.
× *vulpina* (= *axillaris*, Good). Hall Wood, Wood Ditton (Relh.). The wood has disappeared, and the record is therefore doubtful.
C. curta Good 4. Not found since 1860.
C. leporina L. 1, 3, 4, 5.
C. elata All. 1, 3. Nearly always extremely plentiful where it occurs.
(*b*) *turfosa* (Fr.) 1. Welch's Dam (Fryer).
C. gracilis Curt. 1, 2.
var. *prolixa* (Fr.) 1, 2. The type is decidedly local, the variety very rare.
C. Goodenovii Gay. 1, 3, 4, 5.
C. flacca Schreb. 1, 2, 3, 5.
C. pilulifera, L. 3, 4, 5.
C. ericetorum Poll. 3. Gogmagog Hills and Devil's Dyke.
C. caryophyllea Latourr. 1, 3, 4, 5, 6.
C. pallescens L. 1, 3, 5. On chalk at Swaffham Prior (Evans), Sutton Dole Fen, Chippenham Fen (Fryer) and locally on the boulder clay.
C. panicea, L. 1, 2, 3, 4, 5.
C. pendula Huds. 3, 5. Probably extinct in 3.
C. strigosa, Huds. Hall Wood, Wood Ditton (Relh.) is our only record. The wood no longer exists.
C. sylvatica Huds. 1, 2, 3, 5.
C. binervis Sm. 1, 3, 4. Reported also from Croydon (Bab.).

C. distans L. 1, 2?, 3, 4, 5? The typical plant certainly grows near Waterbeach and Foul Anchor (Evans) and at Chippenham Fen (Bennett).
C. fulva Host 1, 2?, 3, 5.
C. flava L. 1, 2, 3, 4.
(*b*) *lepidocarpa* 1.
C. Œderi, Retz 1, 3, 4.
(*d*) *œdocarpa*, And. 1.
C. lasiocarpa Ehrh. 1, 4. (Extinct in 4.)
C. hirta L. 1, 2, 3, 4, 5, 6.
C. Pseudo-Cyperus, L. 1, 2, 3, 5. For 3 we have no recent records. The plant is rare.
C. acutiformis, Ehrh. 1, 3, 4, 5, 6.
(*b*) *Kochiana* (DC.). A form probably referable here has been found at Fen Ditton (1).
C. riparia Curt. 1, 2, 3, 4, 5.
C. inflata Huds. 1, 3, 4.
C. vesicaria L. 1. Observed of late years at Burwell Fen (Bennett), Snailwell Fen (Moss), Sutton and Fen Ditton (Evans), Welch's Dam and Whittlesey (Fryer).

GRAMINACEÆ.

[*Setaria viridis* Beauv. 6. Still occurs at Chippenham Gravel Pits, and has been found at Fordham (Evans).]
[*S. glauca* 1. Welch's Dam and Sutton (Fryer).]
[*Phalaris canariensis* L.]
P. arundinacea L. 1, 2, 3, 4, 5, 6.
Anthoxanthum odoratum L. 1, 2, 3, 4, 5, 6.
Alopecurus myosuroides, Huds. 1, 2.
A. æqualis Sobol. 1, 2, 3?, 5?
A. geniculatus L. 1, 2, 5.
A. pratensis L. 1, 2, 3, 4, 5.
Milium effusum L. 2, 5.
Phleum pratense L. Common.
(*b*) *nodosum* (L.) Chippenham (6), and possibly elsewhere.
P. phleoides Simonkai 3, 6. Still occurs pretty plentifully at the Furze Hills, Hildersham.
P. arenarium L. 3, 6. Newmarket Heath (Rev. J. Hemsted, *Eng. Bot.* tab. 222), Chippenham (Evans).
Agrostis canina L. 1, 4, 5.
A. alba L. Common.
(*b*) *stolonifera* (L.).
A. tenuis Sibth. 1, 2, 3, 4, 5, 6.
Calamagrostis epigeios Roth. 1, 2, 3, 4, 5.
C. canescens Druce 1, 2, 3, 5. Wicken Fen, Chippenham Fen,

Wimblington Firelots, Doddington Wood, Coveney, Witcham, and Gamlingay Wood, are the localities where this species has been recently noticed. It is as common at Wicken as the last species, but has been constantly confounded with it.

Apera Spica-venti Beauv. 4, 5. Not found recently.

A. interrupta Beauv. 3, 6. The record for 3 is that of Mr J. Stratton in 1855 from Pampisford (Babington, *Flora of Cambridgeshire*).

Aira caryophyllea L. 1, 3, 4, 6.

A. præcox L. 1, 3, 4, 6.

Deschampsia cæspitosa, Beauv. 1, 2, 3, 5, 6.

D. flexuosa, Trin. 4.

Holcus mollis L. 1, 2, 4, 5. Chatteris, Doddington, Gamlingay greensand and Wood Ditton.

H. lanatus L. Common.

Trisetum flavescens, Beauv. 1, 2, 3, 4, 5, 6.

Avena pubescens Huds. 1, 3, 5, 6.

A. pratensis L. 1, 2, 3, 5?, 6.

[*A. fatua* L. 1, 2, 3.]

Arrhenatherum elatius Mert. & Koch. Common.

(*b*) *bulbosum* Presl.

Sieglingia decumbens Bernh. 1, 2?, 3, 4, 5?, 6. A record by Newbould from Toft may refer to (2) or (5). The plant is rare in the county.

Phragmites communis Trin. 1, 2, 3, 4, 5, 6.

Cynosurus cristatus L. Common.

Koeleria gracilis Pers.

(*c*) *britannica* Domin. 1, 3, 5, 6.

Molinia cærulea Mœnch. 1, 2?, 3, 4, 5? A record by Newbould from Toft may refer either to (2) or (5).

(*b*) *major* Roth. 1, 4.

(*c*) *depauperata* 1, 4.

Catabrosa aquatica Beauv. 1, 2, 3.

Melica uniflora Retz 5.

Dactylis glomerata L. Common.

Briza media L. 1, 2?, 3, 5, 6.

Poa annua L. Common.

P. nemoralis L. 1, 3, 4, 5.

P. compressa L. 1, 2?, 3, 4, 5, 6.

(*b*) *subcompressa* (Parn.). Probably all the records refer to this form. Many certainly do so.

P. pratensis L. 1, 2, 3, 4, 5, 6.

(*b*) *subcærulea* (Sm.) 3.

P. trivialis L. Common.

Glyceria fluitans Br. Common.

× *plicata* (= *pedicillata* Towns.) 3, 5.

G. plicata Fr. Not uncommon, further details of localities are needed.
G. aquatica Wahlb. 1, 2, 3, 4, 5.
G. maritima. Mert. & Koch 1.
G. distans Wahlb. 1.
Festuca rigida, Kunth. 1, 2, 3, 5, 6.
F. Myuros L. 1, 3, 4.
F. bromoides L. 2, 3, 4, 6.
F. ovina L. 1, 2, 3, 4, 5, 6.
(*d*) *duriuscula* Hackel 1, 3, 4.
F. rubra L. 1, 2?, 3, 4, 5.
F. pratensis Huds. 1, 2?, 3, 5, 6.
× *Lolium perenne* (= *loliacea* Curt.) 1, 2?, 3.
F. elatior L. 1, 2, 3, 5, 6.
Bromus giganteus, L. 1, 2, 3, 5, 6.
B. ramosus Huds. 1, 2, 3, 5, 6.
B. erectus Huds. 2?, 3, 6.
(*b*) *villosus* Bab.
B. sterilis L. Common.
B. secalinus L. 1, 2?, 3, 6.
(*b*) *velutinus* (Schrad.) 1, 2?
B. racemosus L. 1, 3, 4, 5.
B. commutatus Schrad. 1, 2, 3, 4, 5.
B. hordeaceus L. (= *mollis* L.). Common.
[*B. arvensis* L. 1, 5.]
Brachypodium sylvaticum Roem. & Schult. 1, 2, 3, 5, 6.
B. pinnatum Beauv. 1, 2?, 3, 5. Nearly always on the Chalk or Boulder Clay.
Lolium perenne L. Common.
[(*c*) *multiflorum* Lam.]
[*L. temulentum* L. 1, 2?, 3, 5.]
Agropyrum caninum Beauv. 1, 2, 3, 5, 6. Local.
A. repens Beauv. Common.
A. pungens Roem. & Schult. 1.
Lepturus filiformis Trin. 1.
Nardus stricta L. 3, 4. Relhan recorded the plant from Hildersham, and it still occurs at Gamlingay.
Hordeum nodosum L. Common.
H. murinum L. Fairly common.
H. marinum Huds. 1.

II. GYMNOSPERMÆ.

Coniferæ.

Araucariaceæ.

Juniperus communis L. 3. Fleam Dyke.

Taxaceæ.

[*Pinus sylvestris* L.]
Taxus baccata L. Perhaps native in Worts' Causeway Wood on the Gogmagog Hills. It has been dug up in the Fens.

III. PTERIDOPHYTA.

Filicineæ.

Ophioglossaceæ.

Ophioglossum vulgatum L. 1, 2, 3, 4, 5.
Botrychium Lunaria Sw. 3, 6.

Osmundaceæ.

Osmunda regalis L. Gamlingay Park (Ray). Certainly extinct.

Polypodiaceæ.

[*Adiantum Capillus-Veneris* L. 5. Brickwork of platform at Old North Road Station.]
Pteris aquilina L. 1, 3, 4, 5, 6. Native in 4, 5, 6.
Asplenium Adiantum-nigrum L. 1, 2, 3, 5.
A. Trichomanes L. 1, 2, 3, 5.
A. Ruta-muraria L. 1, 2, 3, 5.
Athyrium Filix-fœmina Roth. 2, 4. Not found since 1860.
Phyllitis Scolopendrium Newm. 1, 2, 3, 4, 5. Probably not native.
Polystichum aculeatum Roth. 4 (Gamlingay, T. Martyn).
Lastrea Thelypteris Bory 1. Still plentiful in Wicken Fen.
L. montana T. Moore 4. Gamlingay (Dent).
L. Filix-mas Presl. 1, 2, 3, 4, 5. Decidedly scarce.
L. spinulosa Presl. 3. Fulbourn (Wanton).
L. aristata Rendle & Britten 4, 5.
Polypodium vulgare L. 1, 2, 3, 5. Very rare.

Equisetineæ.

Equisetaceæ.

Equisetum maximum L. 3. Also recorded from Ely (Henslow).
E. arvense L. Common.

E. sylvaticum L. 1, 5. No records since the time of Relhan and T. Martyn.
E. palustre L. 1, 2, 3, 4, 5, 6.
E. limosum L. 1, 2?, 3, 4, 5, 6?
(*b*) *fluviatile* (L.) 1, 2, 5.
E. hyemale L. 1, 4. No records except for Stretham Ferry and Gamlingay, by Relhan.

Lycopodineæ.

Lycopodiaceæ.

Lycopodium inundatum L. 4 (Gamlingay, extinct).
L. clavatum L. 4. Not found since 1860.

CHARACEÆ *.

Chara fragilis, Desv. 1. Mepal, Sutton, Chatteris and Whittlesey (Fryer), Wicken and Burwell (Bennett), Chippenham Fen and West Fen, Ely (W. Cross), Haddenham and Roswell Pits (Bullock-Webster).

var. *Hedwigii* (Ag.), Roswell Pits and Wicken Fen (Bullock-Webster), Sutton (Fryer).

var. *capillacea* (Thuill.), Haddenham (Bullock-Webster), Welch's Dam (Fryer).

subsp. *delicatula* Braun, Wicken Fen (E. F. Linton), Downham Pymore (Bullock-Webster).

C. aspera Willd. 1. Burwell Lode and Wicken Fen (Bullock-Webster), Vermuyden's Drain, Welch's Dam, Chatteris (Fryer).

subsp. *desmacantha* H. & J. Groves. Burwell Fen (Bennett), Quy Fen (Bullock-Webster).

C. polyacantha Braun 1. Horseway, near Chatteris (Fryer), Wicken and Snailwell (Bennett), Chippenham Fen (Cross), Quy Fen (Hill), Stretham, Bottisham and Burwell Fens (Bullock-Webster).

C. contraria. Wicken Fen (H. & J. Groves).

C. hispida L. 1, 2?, 3, 5. Hinton Moor (Relhan), near Fulbourn, Teversham, Shelford, Cambridge, Kingston Wood, Waterbeach, Witcham, Witchford, Bottisham, Wicken and Doddington Fens (Babington's *Flora of Cambridgeshire*), Burwell Fen (Bennett), Chippenham Fen (Babington), Sawston (C. B. Clarke), Roswell Pits and Haddenham (Bullock-Webster), March, Sutton, Welch's Dam, Mepal and Chatteris (Fryer), Burnt Fen (W. M. Hind).

C. vulgaris L. 1, 2?, 3, 4, 5. Cambridge, Brinkley, Sawston Moor, Gamlingay, Hardwick, Toft, Haslingfield, Coton, Swaffham Bulbeck, Witcham, Wicken, Bottisham and Snailwell Fens (Babington, *op. cit.*), Burwell (Bennett), Isleham, Sutton, Mepal, Manea, Welch's Dam, Chatteris and Langwood Fen (Fryer), Roswell Pits, Thetford near Ely, Prickwillow and Chesterton (Bullock-Webster), Waterbeach (Hiern), Nine Wells and Chippenham Fen (Cross).

var. *longibracteata* Kuetz. Fulbourn (H. & J. Groves), Fen Ditton (C. B. Clarke), Ely and Prickwillow (Bullock-Webster), Upware (Bennett).

var. *crassicaulis* Kuetz. Burwell Fen (H. & J. Groves).

var. *papillata* Wallr. Upware (Bennett), Haddenham and Roswell Pits (Bullock-Webster), Soham and Burwell Fen (H. & J. Groves).

* This group has been brought up to date for us by Messrs H. and J. Groves.

Tolypella glomerata Leonh. 1, 3. Welch's Dam, Manea, Mepal and Chatteris Turf Fen (Fryer), Wicken Fen (Bennett), Bottisham Fen and Ely (H. & J. Groves), Sawston (C. B. Clarke), Fulbourn, Nine Wells near Shelford (Bennett).

T. prolifera Leonh. 1. Old West River near Stretham Ferry (Bullock-Webster), Vermuden's Drain near Chatteris, Mepal and Sutton Fen (Fryer). First County Record by A. Fryer, 1882.

T. intricata Leonh. 1. Harston (Bennett), Washes from Sutton to Witcham (Fryer).

Nitella tenuissima Kuetz. 1. Swaffham (ex herb. J. Spode) ? county, Bottisham and Burwell Fens (Babington, *op. cit.*), Wicken Lode (Bennett, plentiful).

N. mucronata Miquel 2. Roswell Pits (Bullock-Webster). First County Record.

N. flexilis Agardh. 1, 2? Lord's Bridge near Barton, Reach Lode, Bottisham Fen (Babington, *op. cit.*), Welney (Fryer).

var. *nidifica* Wallr. With some doubt we refer to this variety a curious monœcious plant occurring about Sutton and Mepal, resembling *N. opaca* in stature and habit, in the size and colour of the antheridia and in the usually somewhat mucronate ultimate rays.

N. opaca Agardh. 1, 4. Wicken (Bennett), Gamlingay (Babington).

N. capitata Agardh. 1. Sutton Gault, in the Washes, and thence in the Old Bedford River to Mepal. First British Record by A. Fryer, 1885.

IV. BRYOPHYTA.

By the Rev. P. G. M. Rhodes, M.A., Pembroke College.

The Bryophyta of Cambridgeshire were investigated as exhaustively as the knowledge of the times permitted at the end of the eighteenth century, by the Rev. R. Relhan, Chaplain of King's College, and others. We are fortunate in possessing this account of the Cambs. moss-flora, dating as it does from a time prior to the drainage of the more important fens, and we are enabled to reconstruct an ancient flora which has now almost entirely vanished. As far as Relhan's work can be tested at present, it appears remarkably reliable and, except for a few cases, chiefly where the synonymy is doubtful, his records are included in the following list. It does not seem certain that in his records from "Newmarket" and "Newmarket Heath" that he confined himself to those portions of the Heath strictly in Cambridgeshire, but it is probable that he included the small patch of Suffolk west of Newmarket, as Cambridge botanists generally have done.

Various editions of Relhan's work were brought out, during the latter part of the eighteenth and the beginning of the nineteenth century; but the account of the Cambs. mosses was but little altered in the later editions. The following list is based chiefly on Relhan's second edition (1802).

Since Relhan's time little work appears to have been done at the Cambs. moss-flora, save sporadically. Professor Henslow, in his *Catalogue of British Plants* (Cambridge, 1829), marked those species which occurred in the county of Cambridge, but it is apparent that he relied almost entirely on Relhan's works for the bryophyta, and his pamphlet has for us little independent value. Later a few isolated records from the county are known, as Mr H. N. Dixon's interesting discovery of *Tortula Vahlii* at Cherry Hinton, but no published list of Cambridgeshire Mosses has come into the writer's hands. A few years ago Mr L. J. Sedgwick and the writer started to work those parts of the county more easily accessible from Cambridge, and succeeded in rediscovering most of Relhan's species, and adding a certain number of new ones. The present list must, however, be regarded as a purely tentative one, as much of the county remains unexplored for Mosses, and there are some curious gaps in the list of species to be filled up. Many of the older records and some of the modern ones were not sufficiently closely localized to admit of their classification under the somewhat minute geological subdivisions of the county now

adopted, so that in this respect especially the following list will be found very incomplete.

Taking a general view of the county, it must be said that the moss-flora is poor. The absence of hard rocks in the county, the dryness of the soil and the close cultivation of the land all militate against the existence of mosses. The moss-flora of the fens, before their drainage, though interesting, does not appear to have been very extensive, while even this has now almost totally perished. The patches of fen now remaining, as at Quy and Chippenham, produce little except patches of *Hypnum cuspidatum*, *H. stellatum*, and forms of *H. aduncum* here and there: *Sphagna* appear to be almost extinct. At Wicken Fen the rank growth of vegetation is unsuitable to the bryophyta, though a careful search among the stems of the *Cladium* will shew stunted specimens of *Mnium affine elatum*, *Fissidens*, *Pellia*, *Lophocolea*; and probably other forms could be added. At Fulbourn there are other remnants of a fen moss-flora, *e.g. Hypnum elodes*; but nowhere in the county is there to be found a rich paludal flora, such as that at Tuddenham, just over the Suffolk border.

Much more interesting is the chalk-flora. On the bare face of every "clunch-pit" *Seligeria* occurs abundantly; on chalky earth in the pits, and on arable land in the chalk districts, most of the gypsophilous Tortulaceæ occur: and on the ancient chalk-turf still surviving on the great dykes may be found abundance of such mosses as *Thuidium abietinum*, *Hypnum chrysophyllum*, *Fissidens collinus*, etc. Botanists visiting the county will find the Cherry Hinton chalk-pits the most easily reached, and also probably the richest: for the old chalk-turf flora they may be especially recommended to visit the eastern half of the Devil's Dyke.

The woods of the county present few species of interest: the greater part are of recent origin, except perhaps those on the boulder clay, which have not been well worked, but do not appear to be rich. Further investigation of our arboreal species is much required.

The considerable patches of sand round Gamlingay and Chippenham are unique in their richness, and produce a flora quite distinct from that of the rest of the county. The bogs at Gamlingay, which afforded many plants of interest in Relhan's time, are now drained.

The following is a list of all mosses known to occur in the county on reliable authority; the records are as far as possible assigned to the correct formation, and the name of the authority for that division is appended (*Rel* = Relhan, S = L. J. Sedgwick, Rs = P. G. M. Rhodes). Old records are italicised. Where the division is not stated, it implies that the record was insufficiently localized.

New county records have been kindly verified by Mr Ingham.

Muscineæ.

Sphagnum. Sphagnum appears to have existed till lately at Burwell and Wicken, and still occurs at Chippenham, but even there it is now nearly extinct. Relhan records two varieties: *Sphagnum latifolium* at *Teversham* (1) and *Gamlingay* (4), *Sphagnum cuspidatum* at *Gamlingay* (4).

Tetraphis pellucida Hedw.	1 *Rel.*
Catharinea undulata W. & M.	*Rel.*, S.
Polytrichum nanum Neck	3 *Rel.*
P. piliferum Schreb.	4 *Rel.*
P. juniperinum Willd.	3 *Rel.*, 4 *Rel.*, Rs.
P. attenuatum Menz (= formosum Hedw.)	4 *Rel.*
P. commune L.	3, 4 *Rel.*
Archidium alternifolium Schp.	4 *Gamlingay Bog*, *Rel.*
Pleuridium subulatum Rabenh.	*Rel.*
Seligeria calcarea B. & S.	3 common *Rel.*, Rs.
Ceratodon purpureus B. & S.	*Rel.*, 6 Rs., etc.
Dicranella heteromalla Schp.	3 *Rel.*, Rs.
D. varia Schp.	3 frequent *Rel.*, Rs.
Dicranum scoparium Hedw.	3 *Rel.*, Rs.; 6 Rs.
Fissidens bryoïdes Hedw.	*Rel.*; Ely, etc., S. Scarce.
F. adiantoïdes Hedw.	1 *Rel.*; Wicken Fen Rs.
	3 *Rel.*, extinct through drainage.
β collinus (Mitt.)	3 Fleam Dyke, etc. Rs., ident. Wm Ingham.
F. taxifolius Hedw.	*Rel.*, 2, 3, 5 Rs.; common.
Grimmia apocarpa Hedw.	*Rel.*, 1 Rs.
G. pulvinata Smith	*Rel.*, 1, 6 Rs., etc.; common.
Rhacomitrium canescens Brid.	4 *Rel.*
Phascum cuspidatum Schreb.	*Rel.*, 2, 3 Rs.
γ Schreberianum Brid.	4 *Gamlingay*, *Rel.*
P. Flœrkeanum Brid.	3 Seven Springs, Shelford, H. N. Dixon.
P. curvicolle Ehrh.	3 *Babraham*, *Rel.*
Pottia recta Mitt.	3 *Rel.*
P. bryoides Mitt.	*Rel.*
P. truncatula Lindb.	*Rel.*; I think common.
P. minutula Lindb.	3 S.
P. lanceolata C. M.	3 common, Rs.
Tortula pusilla Mitt.	3 Rs.
T. ambigua Ångstr.	3 Rs.
T. aloïdes De Not	3 Rs.
T. Vahliana Wils.	3 Cherry Hinton. First found here by Mr H. N. Dixon. Abundant in 1911 Rs. In several spots near the pit, on calcareous road-scrapings thrown under hedge. It is a form closely

	approximating to "*var. subflaccida.*"
T. muralis Hedw.	*Rel.*, 1, 2, 3, 4, 5, 6 Rs.
T. subulata Hedw.	*Rel.*, 2 Rs.
T. mutica Lindb.	1 Grantchester Rs.
T. laevipila Schwaeg.	1, 2, 3 Rs.; frequent, often approaches v. *laevipilaeformis* Limp.
T. intermedia Perb.	1 Rs., S.
T. ruralis Ehrh.	*Rel.*, 3, 5 Rs., etc.
Barbula rubella Mitt.	Recorded for county in the Census Moss Catalogue.
B. fallax Mitt.	2, 3 Rs.
B. rigidula Mitt.	Impington S. Common at St Ives, just in Hunts.
B. convoluta Hedw.	3 *Rel.*, Rs.
B. unguiculata Hedw.	*Rel.*, 1, 3 Rs.
Weissia viridula Hedw.	*Rel.*
W. crispa Mitt.	3 Rs., etc.
Trichostomum flavovirens Bruch.	3 Devil's Dyke Rs. Ident. Wm Ingham.
Eucalypta vulgaris Hedw.	3 S.
Zygodon viridissimus R. Br.	Census Moss Catalogue.
Ulota crispa Brid.	Wood Ditton *Rel.*, 5 *Rel.*
Orthotrichum anomalum Hedw. v. saxatile Milde	1 *Rel.*, Rs. Still occurs on Trumpington and Granchester Churches, where it was noticed by Rel. a century or more ago.
O. Lyellii Hook & Tayl.	5 Rs.
O. affine Schrad.	1 Rs., S.
O. diaphanum Schrad.	1, 3, 6 Rs.
Splachnum ampullaceum L.	1 *Sawston and Teversham Moors Rel.*
	3 *Hinton Moor Rel.*
	4 *Gamlingay Bogs Rel.* Extinct in all these places. May survive at Wicken.
[Ephemerum serratum Hanpe	3 *Newmarket Rel.*
Uncertain if in county.	Needs confirmation.]
Physcomitrium pyriforme Brid.	1, 3 *Rel.*
Funaria hygrometrica Sibth.	1, 3 Rs.
Aulacomnium palustre Schwaeg. = Mnium palustre of *Rel.*	1 *Shelford Moor Rel.*
	4 *Gamlingay Bog Rel.*

Henslow took this for *A. androgynum*, and so some confusion has been caused. No reliable record for *A. androgynum* from the county, though it might occur at Gamlingay.

Bartramia pomiformis Hedw.	4 *Rel.*
Philonotis fontana Brid.	1, 3, 4 *Rel.* Extinct in all known localities. May occur at Wicken.
[Leptobryum pyriforme Wils.	*Hothouse, Botanical Garden, Rel.*
Needs confirmation as a native plant.]	
Webera carnea Sch.	1 *Rel.*, Rs.; 3 *Rel.*
W. nutans Hedw.	4 Rs. Ident. W. Ingham.
Bryum pseudotriquetrum Schwaeg.	1 *Rel.*
	1 *Rel.*
B. bimum Schreb.	1 *Rel.*
B. caespiticium L.	*Rel.*
B. capillare L.	*Rel.*, 1, 3 Rs., etc.
[B. atropurpureum W. & M.	? Ely, S.]
B. argenteum L.	*Rel.*, 1, 4 Rs., etc.
B. roseum Schreb.	3 *Gogs, Rel.*; Hildersham Furze Hills, S.
Mnium affine Bland v. elatum B. & S.	1 Wicken Fen Rs. Ident. Wm. Ingham.
M. cuspidatum Hedw.	*Rel.* Must be scarce.
M. rostratum Schrad.	Madingley *Rel.*
M. undulatum L.	1, 3, 6 Rs.; 5 *Rel.*, A. H. Evans.
M. hornum L.	3, 4 *Rel.*, 5 Rs.
[M. punctatum L.	"*Gogs*" *Rel.* An error?]
Fontinalis antipyretica L.	1 *Rel.*, Rs.; 2 *Rel.*
Cryphaea heteromalla Mohr.	4, 5 *Rel.*
Neckera complanata Hübn.	*Rel.*, 2, 5 Rs.
Homalia trichomanoïdes B. & S.	4 *Rel.*
Leucodon sciuroïdes Schwaeg.	*Rel.*, 3 Rs.; 4 on specimen in Larbalestier's Lichen Herb.
Porotrichum alopecurum Mitt.	*Rel.*, 3 Rs.
Leskea polycarpa Ehrh.	1 S., Rs.
Anomodon viticulosus H. & T.	*Rel.*, Boxworth S., 6 Rs.
Thuidium abietinum B. & S.	3 *Rel.*, Rs.
T. tamariscinum B. & S.	4, 5 Rs.
Climacium dendroïdes W. & M.	4 *Rel.* and *Madingley Rel.*
Camptothecium sericeum Kindb.	*Rel.*, 1, 2, 3, 6 Rs.
C. lutescens B. & S.	2 Rs.; 3 *Rel.*, Rs.
Brachythecium albicans B. & S.	3, 4, 6 Rs.
B. rutabulum B. & S.	*Rel.*, 1, 2, 3, 4, 5, 6 Rs.
B. velutinum B. & S.	*Rel.*, 3 S., 4 Rs.
B. plumosum B. & S.	2 *Rel.*
B. purum Dixon	*Rel.*, 2, 3, 4, 6 Rs.
Eurhynchium prælongum Hobk.	*Rel.*, 3, 4, 5, 6 Rs.
E. swartzii Schp.	2, 3 Rs.
E. striatum B. & S.	*Rel.*; must be scarce.
[E. tenellum Milde	Henslow Catalogue.
Needs confirmation.]	

E. myosuroïdes Schp.	*Rel.*, 5 Rs.
E. rusciforme Milde.	1, etc. *Rel.*
E. confertum Milde.	1, 3 S. Common in woods on Gogs.
Amblystegium serpens B. & S.	*Rel.*, 1 S., 2, 3, 5, 6 Rs.
A. filicinum De Not.	1, 3 *Rel.*, 1, 2 Rs.
β Vallisclausæ Dix.	1 Fulbourn Rs. Ident. Wm Ingham.
Hypnum riparium L.	*Rel.*
H. elodes Spruce	1 Fulbourn S. Ident. Wm Ingham.
H. stellatum Schreb.	1 *Rel.*, Rs.; 2 Rs.; 3 *Rel.*
H. chrysophyllum Brid.	3 frequent Rs.
H. aduncum Hedw. type, small form	1 Fulbourn S., 2 Rifle Range Rs.

[β gracilescens Schp., in the Moss Exchange Club Catalogue, was an error for the preceding.]

η paternum Sanio, type of var. form gracilis	1 Quy Rs. 1 Durnford Fen S.; 2 Rifle Range Rs.

Plants from all the above stations for forms of *H. aduncum* have been submitted to Mr Wm Ingham.

H. fluitans L.	1, 4 *Rel.*
H. cupressiforme, L. type.	*Rel.*, 2, 3, 4, 5, 6 Rs.
β resupinatum Schp.	5 Rs.
θ elatum B. & S.	3 Rs.
H. molluscum Hedw.	3 *Rel.*, Rs.
H. scorpioïdes L.	1 *Sawston Moor*, *Fowlmere*, *Rel.*; 3 *Hinton Moor Rel.*
Extinct in above localities.	May survive at Wicken.
H. cuspidatum L.	*Rel.*, 1, 2, 3 Rs.
H. schreberi Willd.	5 *Rel.*
Hylocomium splendens B. & S.	5 *Rel.*
H. squarrosum B. & S.	3 *Rel.*, Rs.; 4, 6 Rs.
H. triquetrum B. & S.	S., 3 *Rel.*, 6 Rs.

Hepaticae.

The Hepatics of the county are neither abundant nor interesting, and have consequently been much neglected by botanists. A number of common hepatics were recorded by Relhan, and are incorporated in the present list, though a certain amount of doubt must attach to records of such ancient date. A few other Hepaticae are marked in Henslow's *Catalogue* as occurring in Cambs., but on unknown authority. Two localities for Cambs. Ricciaceae are given in the *Moss Exchange Club Report* for 1905. Otherwise no records are to hand save for a few species noticed incidentally

by the writer round Cambridge. It is plain, however, that the county is destitute in the extreme with regard to hepatics; even the commonest species, as *Frullania dilatata*, and *Metzgeria furcata*, only occurring at wide intervals and in small quantity. The drained fens produce no species, and vegetation at Wicken is too rank to produce much, though here a careful search would extend the list a little.

The same abbreviations are used as in the case of mosses.

Riccia glauca L.	1 *Cornfield by road to Histon Rel., Barnwell gravel-pit Rel.*
R. fluitans L.	Henslow Cat.; 1 Chippenham Fen, C. H. Waddell in Moss Exchange Club Report, 1905; Waterbeach, A. Shrubbs.
Ricciocarpus natans Corda.	1 *Sawston and Shelford Moors Rel.*; Chippenham Fen, C. H. Waddell, *ut supra.*
	5 *Pond in Hall Wood, Wood Ditton, Rel.*
Reboulia hemisphærica Raddi.	1 *Fulbourn and Sawston Moors Rel.*
Conocephalum conicum Dum.	1 *Shelford Moor Rel.*, 3 Thriplow Rs.
Lunularia cruciata Dum.	1 *Sawston Moor Rel.*
Marchantia polymorpha L.	1 *Cambridge Rel.* In the Backs?
Sphærocarpus Michelii Bell	1 *Barnwell pit Rel.*
Aneura pinguis Dum.	3 *Hinton Moor Rel.*
	4 *Gamlingay Bogs Rel.* etc.
Metzgeria furcata Lindb.	5? *Wood Ditton, Madingley Rel.*
	4 *Rel.*, 5 Madingley, 6 Rs.
Pellia epiphylla Dum.	1 Trumpington, Wicken, Rs.; 4 *Rel.*
Lophozia turbinata Steph.	3 Cherry Hinton Rs.
Plagiochila asplenioïdes Dum.	*Wood Ditton Rel.*
Lophocolea bidentata Dum.	1 *Rel.*, 1, 4 Rs.
L. heterophylla Dum.	3 or 5, 4, 5 Rs.
Saccogyna viticulosa Dum.	5 *Rel.*
Odontoschisma Sphagni Dum.	4 *Gamlingay Bog Rel.*
Radula complanata Dum.	*Rel.*
Madotheca platyphylla Dum.	3 *Rel.*, 6 Rs.
Frullania Tamarisci Dum.	*Rel.*
F. dilatata Dum.	*Rel.*, 2, 5 Rs.
[Anthocerus punctatus L.	Henslow Cat. Needs confirmation.]

Of the localities mentioned above it may be noted that Sawston, Shelford, Hinton and Gamlingay bogs are entirely or nearly drained, and not likely now to support all the species given.

V. THALLOPHYTA.

ALGÆ.

By G. S. West, M.A., D.Sc., F.L.S., St John's College.

The alga-flora of the east of England has not been so thoroughly investigated as that of the other parts of the country, but all that has been done in this direction tends to shew that two of the large groups of the algæ—the Chlorophyceæ and Myxophyceæ—are very poorly represented in the freshwaters of this part of England. As the members of these large groups give some of the most distinctive features to the alga-flora of any district, much that would be of interest is lacking from the alga-flora of the eastern counties.

Of all the eastern counties which have been partially examined for freshwater algæ, Cambridgeshire has yielded the poorest results. "The Alga-flora of Cambridgeshire," which appeared in six instalments in the *Journal of Botany* from Feb. to July, 1899, incorporated the results of four years' collection and examination of material from various parts of the county. It was doubted in this paper "whether any other county in England, of equal area, possesses so poor an alga-flora," and since that time scarcely any other records have been added.

The geological formations of the county, factors which play such an important part in determining the alga-flora of a district, are particularly unsuitable for the existence of an extensive and varied collection of algæ, although it is highly probable that many good things existed on Gamlingay Heath (situated on the Lower Greensand) prior to the time it was drained. The topography of the county is not sufficiently diversified, and, owing to the general low level, none of the peculiar upland collections can be made, few Myxophyceæ being found, and, comparatively, still fewer Desmids. The scarcity of the latter is remarkable, only ten out of twenty-four British genera being represented, and these but scantily.

The two most fruitful localities for Desmids are undoubtedly the fens at Wicken and Chippenham, each being a small remnant of almost primæval fen; but even these are far from prolific. The small pools on the latter, containing *Chara hispida* and a

reduced form of *Utricularia vulgaris*, yielded some rather striking species, as also did the pools and peaty ditches on Wicken Fen containing *Utricularia vulgaris* and *Castalia alba*. The strange appearance of *Cosmarium anceps*, *C. Pokornyanum*, and *C. Holmiense* at Chippenham is worthy of mention, these species being as a rule entirely confined to upland or subalpine districts, being a marked feature of the dripping carboniferous grits and shales of the Pennine Chain and of similar situations among the older rocks of the Lake District, North Wales, etc. They are notably absent from the south-eastern counties of England, and to them may be added *C. speciosum*, which may be placed in the same category, although it is found in Epping Forest, Essex. Roswell Pits, Ely, was found to be a locality productive beyond the average, and not a few uncommon species were obtained from Dernford Fen, about one mile south of Shelford. The chalk districts of the south-east of the county yield practically no algæ, and the numerous ditches and drains of the northern and central parts—many of the larger of which have been in existence since the seventeenth century—exhibit a monotony which could only be found in a low-lying level country. The entire absence of submerged *Sphagnum* and *Sphagnum* bogs causes a corresponding absence of many forms of algæ, and especially certain Desmids, which are more or less exclusively found in such localities. Some of these, such as *Cylindrocystis Brebissonii*, *Closterium striolatum*, *Tetmemorus granulatus*, *Micrasterias truncata*, *Euastrum binale*, *Staurastrum margaritaceum*, etc., are really common and widely distributed species throughout the British Isles, and their absence from Cambridgeshire is therefore all the more noteworthy.

On the whole the Diatoms may be considered as moderately representative, although most of the upland forms are naturally lacking, and there is a marked absence of species belonging to the genera *Eunotia* and *Melosira*. A few of the upland species occur at Wicken and Chippenham Fens, such as *Achnanthidium flexellum*, *Epithemia Argus* var. *alpestris*, and *Eunotia biceps*. These are analogous in their distribution to those Desmids (*Cosmarium anceps*, *C. Pokornyanum*, and *C. Holmiense*) previously mentioned, and the presence of these species in the marshes of a flat country only about ten feet (or less) above the sea-level is very curious, as their natural home is amongst the mosses and algæ of the rocky ghylls and glens of the mountainous portions of the British Isles and other parts of Europe. A parallel to this is found in the occurrence of *Cetraria islandica* (Iceland Moss) on some of the Lincolnshire heaths.

The smaller ditches and ponds of the county yield a fair assortment of Zygnemaceæ and Œdogoniaceæ, but the boggy ditches and peaty pools of the fens are mostly disappointing.

They contain for the most part a mixture of the commoner pond species with a very few bog species. Some of the small boggy pools in Chippenham Fen were a little more productive, especially those containing small quantities of a *Utricularia* which appeared to be an unusual form of *U. minor*.

The only characteristic algal associations were those in the large lodes and drains. In these situations, among tangled and floating masses of *Potamogetons* and other aquatic macrophytes, certain algæ occur in more or less profusion, chiefly in the summer and early autumn. These are mostly unicellular Chlorophyceæ and Diatoms. The most abundant and important species were *Cosmarium biretum, C. Turpinii, C. Botrytis, C. impressulum, C. humile, C. subprotumidum* var. *Gregorii, Closterium moniliferum, Cœlastrum sphæricum, C. pulchrum, Pediastrum Boryanum, Scenedesmus obliquus, Cocconeis Placentula, C. Pediculus,* and *Cymatopleura Solea*.

There is a great scarcity of the subaerial species from the alga-flora of Cambridgeshire, and especially of the algal associations so characteristic of wet and dripping rocks, the combined algæ and bryophytes of which so often give a character not only to the flora but to the scenery.

Notwithstanding the poorness of the general alga-flora, there are some very good things found in Cambridgeshire in the way of algæ. The Œdogoniaceæ are fairly well represented, and no doubt there are two or three times as many species yet remaining to be identified when they can be obtained in the proper fruiting condition.

In the Ulotrichaceæ special mention should be made of *Radiofilum flavescens,* which is the only known species of the genus in the British Islands, and as yet has not been found outside Cambridgeshire. *Gongrosira stagnalis* is an interesting member of the Trentepohliaceæ which occurred at Sutton on the shells of *Limnæa peregra*. Of the Zygnemaceæ *Mougeotia paludosa, M. elegantula,* and *Spirogyra pellucida* are the pick, and of the Desmidiaceæ *Mesotœnium Kramstai, Closterium laterale, C. peracerosum, Cosmarium costatum, C. basilicum,* and *Staurastrum paxilliferum* are worthy of special mention. *Nephrocytium obesum* and *Characiopsis turgida* are also noteworthy species. Among the blue-green algæ *Oscillatoria proboscidea, O. acuminata, O. decolorata,* and *Glœochœte Wittrockiana* are the choice species, while among the Diatoms a curious variety of *Synedra Acus* and a much crinkled species of *Eunotia* require further investigation.

The total number of algæ known to occur in Cambridgeshire is about 400 species and 45 varieties.

The localities where mentioned are arranged under the eight areas into which the county is divided by Babington in his *Flora*

*of Cambridgeshire**. These areas are certainly convenient, but hardly natural, and have little or no significance with regard to the distribution of the algæ; they are as follows: 1. Cambridge; 2. Royston; 3. Wimpole; 4. Cottenham; 5. Burwell; 6. Ely; 7. Chatteris; 8. Wisbech. The first two are the least productive, the Cambridge area being a particularly barren one.

The county is by no means well investigated; those Œdogoniaceæ and Zygnemaceæ which have not been obtained in proper fruiting condition (and there are many of them) are not recorded, and there are whole districts, such as Wisbech and Whittlesey, from which no collections have been made.

Class **FLORIDEÆ.**

Order Nemalionaceæ.

Batrachospermum moniliforme (Roth) Ag. 3. Cherryhinton (in ditch), and Seven Springs, Shelford (*Dixon*). 5. Brook at Fulbourn (near the Fleam Dyke) (*Dixon*).

Chantransia chalybea (Lyngb.) Fries. 3. Sheep's Green, Cambridge: June, 1898; growing on *Amblystegium riparium* at the mill-race.

Class **CHLOROPHYCEÆ.**

Order Œdogoniales.

Bulbochæte sessilis Wittr. Forms with large oogonia. 5. Wicken Fen: Aug. 1898.

B. crassiuscula Nordst. [Inclus. *B. ellipsospora* G. S. West, "Alga-fl. Cambs." 1899, p. 55, t. 394, f. 1, 2.] 6. Roswell Pits, Ely; among *Utricularia vulgaris*, July, 1898.

B. subsimplex Wittr. 7. Ponds near March.

B. rectangularis Wittr. 5. Wicken Fen; Chippenham Fen.

Œdogonium curvum Pringsh. 3. Wimpole Park.

Œ. fragile Wittr. 7. Ponds S. of March.

Œ. pyrulum Wittr. var. obesum Wittr. 2. Dernford Fen, 1 mile S. of Shelford.

Œ. vernale (Hass.) Wittr. 2. Dernford Fen, 1 mile S. of Shelford.

Œ. Vaucherii (Le Cl.) A. Br. 3. Wimpole Park.

Œ. oblongum Wittr. Sheep's Green, Cambridge.

Œ. Rothii (Le Cl.) Pringsh. 2. Dernford Fen, 1 mile S. of Shelford.

Œ. undulatum (Bréb.) A. Br. var. Moebiusii Schmidle. 5. Chippenham Fen.

Œ. crassiusculum Wittr. var. idioandrosporum Nordst. & Wittr. [= *Œ. crassipellitum* G. S. West, "Alga-fl. Cambs." 1899, p. 55, t. 394, f. 3—5.] 8. Twenty-foot River, between March and Guyhirn; July, 1898.

* As in Dr West's original paper, cited on p. 259.

Œ. Boscii (Le Cl.) Bréb. 3. Sheep's Green, Cambridge.

Œ. Landsboroughii (Hass.) Kütz. 2. Dernford Fen, 1 mile S. of Shelford.

Order Chætophorales.

Coleochæte scutata Bréb. Generally epiphytic on aquatic phanerogamous plants, and probably abundant, though easily overlooked. 3. Hardwick; Wimpole Park. 6. Roswell Pits, Ely. 7. In ponds near March. 8. In ponds, Guyhirn, attached to *Vaucheria dichotoma*.

C. irregularis Pringsh. Rare. 5. Pools, Chippenham Fen, attached to the submerged stems of *Phragmites communis*. 8. In ponds, Guyhirn, attached to *Myriophyllum*.

Herposteiron confervicola Näg. [= *Aphanochæte repens* A. Br.] 2. Dernford Fen. 3. Sheep's Green, Cambridge; Lord's Bridge; Wimpole Park. 5. Fordham. 6. Roswell Pits, Ely; and ponds near Ely.

Very fine specimens were observed on *Elodea canadensis*, thickly covering both faces of the leaves, the procumbent branches of the alga in some cases closely following the contours of the cells of the *Elodea*, and for this reason exhibiting a marked reticular character. In some of the examples hypnospores were present.

H. pilosissima (Schmidle) G. S. West. [= *Alphanochæte pilosissima* Schmidle.] 3. Wimpole Park, attached to *Œdogonium* sp.

Ulothrix subtilis Kütz. 5. Chippenham Fen.

Var. variabilis (Kütz.) Kirchn. 1. Cambridge. 3. Coton; Wimpole Park.

U. tenuis Kütz. 3. Wimpole Park.

U. moniliformis Kütz. 5. Chippenham Fen.

Radiofilum flavescens G. S. West. 5. Wicken Fen; Aug. 1898. Length of cells 5·5—8·5 μ; breadth of cells 7·5—10·5 μ.

This plant is the only recorded British species of the genus, and has not been seen since its original discovery in 1898. It is distinguished from the only other species of the genus—*R. conjunctivum* Schmidle—by its more elongated and flexuose filaments, its larger elliptical cells which are not apiculate, and by the colour of the older plants.

Stichococcus bacillaris Näg. 1 and 3. On old wood and damp ground, not uncommon about Cambridge; Orwell, on damp stones and wood.

Cylindrocapsa geminella Wolle, var. minor Hansg. Very scarce. 3. Sheep's Green, Cambridge. 6. Roswell Pits, Ely. Crass. cell. veget. 15 μ. *Distrib.*—Bohemia and United States.

Chætophora pisiformis (Roth) Ag. 1. In ditch, Trumpington. 3. Sheep's Green, Cambridge; Hardwick. 7. Near March.

C. incrassata (Huds.) Hazen. [= *C. Cornu Damæ* (Roth) Ag.; *C. endiviæfolia* auct.] 3. Sheep's Green, Cambridge; Hardwick.

C. elegans (Roth) Ag. 6. Near Ely.

Draparnaudia plumosa (Vauch.) Ag. 6. Roswell Pits, Ely.

Myxonema tenue (Ag.) Rabenh. [= *Stigoclonium tenue.*] 3. Sheep's Green, Cambridge.

M. FASTIGIATUM (Kütz.) ——. 3. Wimpole Park.

MICROTHAMNION KÜTZINGIANUM Näg. 5. Wicken Fen: Aug. 1898, amongst *Chara hispida*.

GONGROSIRA STAGNALIS (G. S. West) Schmidle. [= *Pilinia stagnalis* G. S. West, "Alga-fl. Cambs." 1899, p. 107, t. 394, f. 6—9.] 7. The Washes, Sutton, forming a tough dull green stratum on the shells of *Limnæa peregra*.

This is the largest species of the genus, and so far has not been recorded from any other part of the British Islands.

Order ULVALES.

ENTEROMORPHA INTESTINALIS (L.) Link. This plant appears to be generally distributed in the rivers and drain-dykes throughout the county. 3. R. Cam, Sheep's Green. 4. R. Cam at Baitsbite. 5. Burwell Lode. 6. R. Ouse, Ely; Sutton and Mepal, in ponds. 7. The Washes, Sutton; Old River Nene, March. 8. Guyhirn.

Order SCHIZOGONIALES.

PRASIOLA CRISPA (Lightf.) Ag. 1. Trumpington Street, Cambridge.

P. PARIETINA (Vauch.) Wille. [= *Hormidium parietinum* Kütz.] 1. Frequent about Cambridge. 5. Burwell. 7. March.

Order MICROSPORALES.

MICROSPORA FLOCCOSA (Vauch.) Thur. 3. Sheep's Green, Cambridge.

Order CLADOPHORALES.

CLADOPHORA CRISPATA (Roth) Kütz. 2. Dernford Fen, 1 mile S. of Shelford. 3. Comberton; Wimpole Park. 4. Pond near Girton. 6. Roswell Pits, Ely. 7. Near March.

C. GLOMERATA (L.) Kütz. 3. R. Cam at Cambridge; Coton. 6. Near Ely.

C. FLAVESCENS Ag. 2. Octagon Pond, Wimpole Park. 8. Sheep's Green, Cambridge. 7. Sutton West Fen.

RHIZOCLONIUM HIEROGLYPHICUM Kütz. 2 Dernford Fen, 1 mile S. of Shelford; Octagon Pond, Wimpole Park. 3. Sheep's Green, Cambridge. 6. In ponds near Ely. 7. Sutton West Fen. 8. In ditches near Guyhirn. Frequent, May to Aug.

Order SIPHONEÆ.

VAUCHERIA SESSILIS (Vauch.) DC. 3. Sheep's Green, Cambridge; Orwell; Wimpole Park. 5. Chippenham Fen. 8. Guyhirn. In a gathering of this species from Sheep's Green, Cambridge, in July, 1898, some curious globular swellings were noticed at intervals in many of the filaments, frequently situated quite close to the oogonia, and generally giving rise to one or more branches of varying length. They were most probably "galls" produced by one of the Rotifera.

V. DICHOTOMA (L.) Ag. 4. River Cam, between the "Pike and Eel" and Baitsbite. 5. Burwell Lode. 8. In ponds, Guyhirn.

V. TERRESTRIS Lyngb. 2. Great Shelford, by the roadside. 6. Near Ely, on damp ground.

Order CONJUGATÆ.

MOUGEOTIA SCALARIS Hass. 6. Roswell Pits, Ely: July, 1898.

M. PARVULA Hass. 6. Roswell Pits, Ely. 7. In ditches near March. This species is somewhat scarce in the county. Conjugating examples but without ripe spores, from Chippenham Fen.

M. GENUFLEXA (Dillw.) Ag. [*Mesocarpus pleurocarpus* De Bary; *Mougeotia mirabilis* (A. Br.) Wittr.] 2. Dernford Fen, 1 mile S. of Shelford. 3. Sheep's Green, Cambridge; Hardwick. 6. Roswell Pits, Ely. 7. Sutton West Fen; in ditches about March. 8. Guyhirn. Frequently met with in a possible state of conjugation, but not with mature spores.

M. PALUDOSA G. S. West. 5. Burwell Lode, abundant: Aug. 1898. This species is as yet only known to occur in Cambridgeshire.

M. CALCAREA Wittr. 5. Wicken Fen: Aug. 1900.

M. VIRIDIS (Kütz.) Wittr. 3. Hardwick. 5. Chippenham Fen.

M. GRACILLIMA (Hass.) Wittr. 3. Sheep's Green, Cambridge. 5. Wicken Fen.

M. ELEGANTULA Wittr. Diam. veg. cells 4 μ. 5. Chippenham Fen; Wicken Fen. This species was not observed in the conjugating state; but the extreme slenderness of the sterile cells, which were thirty to thirty-five times longer than their diameter, does not admit of its being any other species. Moreover, the chromatophores were restricted to the median portion of the cells exactly in the manner figured by Wittrock. *Distrib.*—Westmoreland, West Ireland, and Sweden.

DEBARYA CRUCIATA Price. 3. Coe Fen. The description of this species requires revision as the original is very erroneous and misleading.

ZYGNEMA CRUCIATUM (Vauch.) Ag. 3. Wimpole Park: June, 1898. Sterile examples of a *Zygnema*, which was probably this species, were observed from the ditch by the Botanical Gardens, and from Sheep's Green, Cambridge.

Z. ERICETORUM (Kütz.) Hansg. [*Zygogonium ericetorum* Kütz.] 5. Chippenham Fen, the aquatic form [forma *fluitans* (Kütz.) Rabenh.], abundant, Aug. 1898.

Z. RALFSII (Hass.) De Bary. 3. Chippenham Fen. The zygospores were rather larger than the average size for this species.

SPIROGYRA ARCTA (Ag.) Kütz. var. CATÆNIFORMIS (Hass.) Kirchn. [*S. catæniformis* (Hass.) Kütz.] 6. Roswell Pits, Ely.

S. VARIANS (Hass.) Kütz. 2. Dernford Fen, 1 mile S. of Shelford. 5. Chippenham Fen. 6. In ponds near Ely.

S. COMMUNIS (Hass.) Kütz. 6. Ditches near Ely.

S. NITIDA (Dillw.) Link. 6. Ditches near Ely.

S. MAJUSCULA Kütz. [*S. orthospira* Näg.] 5. Chippenham Fen: very fine, Aug. 1898.

S. MAXIMA (Hass.) Wittr. Syn. *S. orbicularis* (Hass.) Kütz. 6. Roswell Pits, Ely: July, 1898. The ripe zygospores are of the

same rich brown colour as those of *S. majuscula*, and, although they are of considerably greater diameter, the spore-wall is comparatively thinner. The proportion of the thickness of the spore-wall to the diameter of the ripe spore is as 1 : 17·44 ; in the case of *S. majuscula* it is as 1 : 12·5.

S. GRACILIS (Hass.) Kütz. 3. Sheep's Green, Cambridge ; Wimpole Park.

S. PELLUCIDA (Hass.) Kütz. [*Zygnema pellucida* Hass.] 1. Ditch by the Botanical Gardens, Cambridge : June, 1897, intermingled with *S. bellis*. 3. Sheep's Green, Cambridge : Aug. 1898. *Distrib.*— England (Herefordshire ; Yorkshire !).

S. BELLIS (Hass.) Cleve. 1. In the ditch by the Botanical Gardens, Cambridge : June, 1897, intermingled with *S. pellucida* (Hass.) Kütz.

S. GREVILLEANA (Hass.) Kütz. 3. Sheep's Green, Cambridge ; Hardwick, in ponds.

GONATOZYGON RALFSII De Bary. 5. Chippenham Fen, amongst *Utricularia vulgaris* ; Wicken Fen, amongst *Myriophyllum spicatum*. 6. Roswell Pits, Ely.

G. BRÉBISSONII De Bary. 6. Roswell Pits, Ely.

G. KINAHANI (Arch.) Rabenh. 3. Sheep's Green, Cambridge : in pond amongst *Spirogyra* sp., July, 1898.

MESOTÆNIUM KRAMSTAI Lemmerm. 5. Chippenham Fen, in small pools amongst *Utricularia vulgaris* : Aug. 1898. This species, the most elongate of the genus, was discovered by Lemmermann in Aug. 1895, in small pools on the "Riesengebirge," between Bohemia and Prussian Silesia. The Cambridgeshire specimens were of variable length, and all had the poles truncately rounded ; certainly more truncate than figured by Lemmermann. All the examples observed were packed with a reserve of fatty oil, as is so often the case in species of this genus.

PENIUM DIGITUS (Ehrenb.) Bréb. 7. Ponds S. of March.

P. sp. Only one specimen of this species was observed ; the cell was oblong-elliptical, with semicircular poles, and in the middle there was a faint constriction. 8. Guyhirn.

P. CRUCIFERUM (De Bary) Wittr. [*Cosmarium cruciferum* De Bary.] 5. Chippenham Fen.

CLOSTERIUM ACEROSUM (Schrank) Ehrenb. 2. Dernford Fen, 1 mile S. of Shelford. 3. Hardwick ; Lord's Bridge. 5. Wicken Fen.

Var. ANGOLENSE West & G. S. West, *l. c.* 6. Roswell Pits, Ely. Long. 773 μ ; lat. 30 μ.

C. LATERALE Nordst. 2. Dernford Fen, 1 mile S. of Shelford. Since the original discovery of this rare species of *Closterium* at Pasto de Olaria, Pirassununga, Brazil, in Jan. 1880, it has not been placed on record for any other locality, and its extraordinary occurrence in Cambridgeshire is deserving of particular mention.

The other species of *Closterium* known to occur in Cambridgeshire are the following :—*Cl. lanceolatum* Kütz., *Cl. lunula* Nitzsch, *Cl. prælongum* forma *brevior* West, *Cl. gracile* Bréb., *Cl. peracerosum* var. *elegans* G. S. West, *Cl. Pritchardianum* Arch., *Cl. lineatum* Ehrenb.,

Cl. rostratum Ehrenb., *Cl. Kützingii* Bréb., *Cl. pronum* Bréb., *Cl. aciculare* var. *subpronum* W. & G. S. West, *Cl. acutum* (Lyngb.) Bréb., *Cl. Ehrenbergii* Menegh., *Cl. Malinvernianum* De Not., *Cl. moniliferum* (Bory) Ehrenb., *Cl. Leibleinii* Kütz., *Cl. Dianæ* Ehrenb., *Cl. parvulum* Näg., *Cl. Venus* Kütz., *Cl. Jenneri* var. *robustum* G. S. West, and *Cl. idiosporum* W. & G. S. West (Wicken Fen).

Pleurotænium coronatum (Bréb.) Rabenh. var. nodulosum (Bréb.) West. 5. Chippenham Fen.

Pl. Trabecula (Ehrenb.) Näg., and forma *granulata*; also various forms of *Pl. Ehrenbergii*.

Euastrum insulare (Wittr.) Roy. 5. Wicken Fen.

Cosmarium costatum Nordst. 5. Chippenham Fen. This rare species has up to the present only been recorded for the British Isles from several localities in Scotland, Yorkshire, and North Wales; and its occurrence in the fens of the east of England is most unaccountable, being strictly comparable to those cases of *C. anceps*, *C. Holmiense*, &c., already mentioned.

C. basilicum G. S. West. 5. Chippenham Fen: Aug. 1898. This species is not known to occur elsewhere in the British Islands.

C. subprotumidum Nordst. var. Gregorii (Roy & Biss.) W. & G. S. West. 7. The Washes, Sutton, and Sutton West Fen. 8. Twenty-foot River, between March and Guyhirn.

C. subcostatum Nordst. 6. Roswell Pits, Ely.

Var. Beckii (Gutw.) W. & G. S. West. 8. Guyhirn, in ponds.

C. anceps Lund. 5. Chippenham Fen, abundant in a ditch: Aug. 1898.

C. Pokornyanum (Grun.) W. & G. S. West. [= *C. angustatum* (Wittr.) Nordst.] 5. Chippenham Fen.

The occurrence of this species and the preceding one in the fens of the east of England is very remarkable.

C. protuberans Lund. forma padulosa W. & G. S. West. [= *C. protuberans* forma G. S. West, "Alga-fl. Cambs." p. 116, t. 394, f. 12.] 5. Chippenham Fen, in ditches.

The following species of *Cosmarium* also occur in Cambridgeshire:—*C. quadratum* Ralfs, *C. Holmiense* Lund. var. *integrum* Lund., *C. granatum* Bréb. and var. *subgranatum* Nordst., *C. subtumidum* Nordst. var. *Klebsii* (Gutw.) W. & G. S. West, *C. bioculatum* Bréb., *C. abbreviatum* Racib., *C. Regnellii* Wille, *C. impressulum* Elfr., *C. læve* Rabenh. var. *septentrionale* Wille and var. *octangulare* (Wille) W. & G. S. West, *C. Meneghinii* Bréb., *C. angulosum* Bréb., *C. difficile* Lütkem., *C. exiguum* Arch., *C. humile* (Gay) Nordst. and var. *substriatum* (Nordst.) Schimdle, *C. tetraopthalmum* Menegh., *C. margaritatum* (Lund.) Roy & Biss., *C. margaritiferum* (Turp.) Menegh., *C. reniforme* (Ralfs) Arch. and var. *compressum* Nordst., *C. punctulatum* Bréb., *C. formosulum* Hoff, *C. quinarium* Lund., *C. præmorsum* Bréb., *C. Botrytis* (Bory) Menegh. and var. *mediolæve* West, *C. Turpinii* Bréb., *C. biretum* Bréb., *C. ochthodes* Nordst. and var. *subcirculare* Wille, and *C. speciosum* Lund.

Staurastrum apiculatum Bréb. 5. Wicken Fen.

S. PAXILLIFERUM G. S. West. 5. Wicken Fen: Aug. 1898. A rare British species only known to occur elsewhere in N. Yorkshire.

S. AVICULA Bréb. Most of the forms observed were finely granulate, and the spines at the angles were reduced. 6. Roswell Pits, Ely.

S. ORBICULARE (Ehrenb.) Ralfs var. DEPRESSUM Roy & Biss. 2. Dernford Fen, 1 mile S. of Shelford. 5. Wicken Fen.

S. PUNCTULATUM Bréb. 5. Wicken Fen. A form with the lateral angles in the front view slightly produced. 2. Dernford Fen, 1 mile S. of Shelford.

S. HEXACERUM (Ehrenb.) Wittr. [*S. tricorne* Ralfs.] 6. Roswell Pits, Ely.

S. INFLEXUM Bréb. 2. Dernford Fen, 1 mile S. of Shelford. 5. Wicken Fen; Chippenham Fen.

S. CRENULATUM (Näg.) Arch. 2. Dernford Fen, 1 mile S. of Shelford.

HYALOTHECA DISSILIENS (Sm.) Bréb. 5. Wicken Fen; Chippenham Fen.

Order PROTOCOCCOIDEÆ.

GONIUM PECTORALE Müller. 3. In ditch, St John's College "backs," Cambridge; Sheep's Green, Cambridge. 5. Burwell Lode.

PANDORINA MORUM (Müll.) Bory. 3. Sheep's Green, Cambridge; Hardwick. 6. Roswell Pits, Ely. 7. The Washes, Sutton; ditches and pools about March, in immense quantity: Aug. 1898.

CHLAMYDOMONAS PULVISCULUS (Müll.) Ehrenb. 5. Chippenham Fen. 6. In ponds near Ely. 7. Near March; Sutton West Fen.

SPHÆRELLA LACUSTRIS (Girod.) Wittr. [= *Hæmatococcus lacustris* (Girod.) Rostaf.; *Chlamydococcus pluvialis* (Flot.) A. Br.] 5. Wicken Fen. 6. Roswell Pits, Ely.

CŒLASTRUM CUBICUM Näg., *C. sphæricum* Näg., *C. cambricum* Arch. [= *C. pulchrum* Schmidle.]

Pediastrum Boryanum (Turp.) Menegh. and var. *granulatum* (Kütz.) A. Br., *P. constrictum* Hass., *P. duplex* Meyen, *P. Tetras* (Ehrenb.) Ralfs, *P. integrum* Näg.

CRUCIGENIA RECTANGULARIS (Näg.) A. Br. 5. Wicken Fen, very fine, 1896 and 1898. 6. Roswell Pits, Ely.

C. QUADRATA Morren. 5. Chippenham Fen: families of sixteen cells. 7. The Washes, Sutton.

CHÆTOSPHÆRIDIUM GLOBOSUM (Nordst.) Klebahn. [= *Nordstedtia globosa* Borzi.] 3. Hardwick.

Scenedesmus bijugatus (Turp.) Kütz., *S. quadricauda* (Turp.) Bréb. and var. *abundans* Kirchn., *S. alternans* Reinsch, *S. obliquus* (Turp.) Kütz. [and *Dactylococcus infusionum* Näg.], *S. antennatus*, *S. denticulatus* Lagerh. var. *linearis* Hansg., and *S. acutiformis* Schröder.

Ankistrodesmus falcatus (Corda) Ralfs and var. *aciculare* (A. Br.) G. S. West, and *A. convolutus* (Rabenh.) G. S. West.

Tetraëdron minimum (A. Br.) Hansg., *T. trigonum* (Näg.) Hansg., *T. muticum* (A. Br.) Hansg., *T. caudatum* (Corda) Hansg., *T. regulare* Kütz., and

T. TETRAGONUM (Näg.) Hansg. var. INERME Wille. Small forms: diam. 13·5—18·5 μ; thickness 9·5 μ. 5. Chippenham Fen.

CERASTERIAS LONGISPINA (Perty) Reinsch. [*Polyedrium longispinum* Perty.] 3. Ditch, St John's College "backs," Cambridge.

CHARACIUM SUBULATUM A. Br. 3. Wimpole Park.

C. MINUTUM A. Br. 2. Dernford Fen, 1 mile S. of Shelford.

C. AMBIGUUM Herm. 5. Wicken Fen. 6. Near Ely.

C. HETEROMORPHUM Reinsch. [*Hydrianum heteromorphum* Reinsch.] 3. Sheep's Green, Cambridge; Hardwick. 5. Wicken Fen.

C. LONGIPES Rabenh. 3. Sheep's Green, Cambridge.

C. ORNITHOCEPHALUM A. Br. 5. Wicken Fen.

CHLOROCHYTRIUM LEMNÆ Cohn. 6. Near Sutton, on *Lemna trisulca*.

SCHIZOCHLAMYS DELICATULA West. 5. Sheep's Green, Cambridge: June, 1895. 5. Chippenham Fen: Aug. 1898.

APIOCYSTIS BRAUNIANA Näg. 2. Dernford Fen, 1 mile S. of Shelford: Aug. 1898, very fine. 3. Hardwick. 5. Wicken Fen. 6. Roswell Pits, Ely.

TETRASPORA GELATINOSA (Vauch.) Desv. 1. In the ditch by the Botanical Gardens, Trumpington Road, Cambridge: June, 1897.

BOTRYOCOCCUS BRAUNII Kütz. [Inclus. *Ineffigiata neglecta* W. & G. S. West.] 2. Dernford Fen (very abundant in Aug. 1898). 3. Sheep's Green, Cambridge; Wimpole Park. 5. Wicken Fen. 6. Roswell Pits, Ely. 7. Ponds S. of March; The Washes, Sutton, and Sutton West Fen. 8. Twenty-foot River between March and Guyhirn.

NEPHROCYTIUM LUNATUM West. 2. Dernford Fen, 1 mile S. of Shelford. 6. Roswell Pits, Ely: fairly abundant, Aug. 1895, and July, 1898. *Distrib.*—Westmoreland! Yorkshire! Surrey! N. Ireland! Paraguay.

N. NAGELII Grun. 5. Chippenham Fen; Wicken Fen. 6. Roswell Pits, Ely. 7. Ponds S. of March.

N. OBESUM West. 5. Chippenham Fen. *Distrib.*—Cumberland! Brazil. Paraguay.

Two forms of this species were noticed in addition to the type. One had somewhat narrower cells with the cell-membrane slightly thickened at the sides. The other was a large form with a very thick integument.

OOCYSTIS SOLITARIA Wittr. 5. Chippenham Fen; Wicken Fen. 8. Guyhirn, in ponds; Twenty-foot River, between March and Guyhirn.

O. PARVA West & G. S. West. 8. Guyhirn.

GLŒOCYSTIS GIGAS (Kütz.) Lagerh. [*Chlorococcum gigas* (Kütz.) Grun.; *Glœocystis ampla* (Kütz.) Rabenh.] 5. Wicken Fen; Chippenham Fen. 6. Roswell Pits, Ely. 7. Ponds S. of March.

G. VESICULOSA Näg. 2. Dernford Fen, 1 mile S. of Shelford 8. Guyhirn, in ditches.

ASTEROCOCCUS SUPERBUS (Cienk.) Scherffel. [= *Glœocystis infusiona* (Schrank) W. & G. S. West.] 5. In ditches, Burwell Lode; Wicken Fen.

Pleurococcus vulgaris Menegh. Abundant in most localities, and very finely developed on some of the hedges.

P. rufescens (Kütz.) Bréb. 1. Very fine on a wet spout, Cambridge: June, 1898.

P. nimbatus De Wildem. 2. Dernford Fen, 1 mile S. of Shelford, attached to leaves of *Nuphar luteum*. 5. Wicken Fen, attached to leaves of *Nymphæa alba*.

Trochiscia hirta (Reinsch) Hansg. 1. Forming dark green masses on damp ground at the bases of trees, Cambridge, along with *Stichococcus bacillaris* Näg.

T. reticularis (Reinsch) Hansg. 5. Chippenham Fen.

Protoderma viride Kütz. 2. Dernford Fen, 1 mile S. of Shelford, on *Cladophora crispata*. 3. Sheep's Green, Cambridge, on *Elodea canadensis*. 5. Burwell Lode, on *Glyceria fluitans*. 7. The Washes, Sutton, on *Glyceria fluitans*.

This alga occurs as an epiphyte on the leaves of many aquatic phanerogams, forming a closely adherent subparenchymatous stratum, which is generally fringed by filamentous outgrowths of unequal extent.

Class **HETEROKONTÆ.**

Order Confervales.

Characiopsis turgida W. & G. S. West. [= *Characium* sp. G. S. West, "Alga-fl. Cambs." 1899, p. 222, t. 395, f. 7.] A large stout species found on several occasions in the ponds on Sheep's Green, Cambridge.

Mischococcus confervicola Näg. 3. Sheep's Green, Cambridge: June, 1898.

Chlorobotrys regularis (West) Bohlin. [= *Glœocystis regularis* W. & G. S. West.] 5. Wicken Fen, in peaty pools.

Ophiocytium cochleare (Eichw.) A. Br. 3. Sheep's Green, Cambridge; Harlton; Hardwick. 5. Burwell; Wicken Fen. 6. Roswell Pits, Ely. 7. Near March.

O. parvulum (Perty) A. Br. 3. Wimpole Park. 5. Chippenham Fen. 8. Guyhirn.

O. Arbuscula (A. Br.) Rabenh. [*Sciadium Arbuscula* A. Br.] 3. Sheep's Green, Cambridge. 6. Roswell Pits, Ely.

Tribonema bombycina (Ag.) Derb. & Sol. [= *Conferva bombycina* Ag.] 3. Sheep's Green, Cambridge; Harlton; Wimpole Park. 5. Burwell; Chippenham Fen. 6. Roswell Pits, Ely; Sutton. 8. Guyhirn.

Forma minor (Wille.) G. S. West. 3. Harlton. 5. Burwell; Wicken Fen.

T. affinis (Kütz.) G. S. West. 3. Sheep's Green, Cambridge: July, 1898.

Botrydium granulatum (L.) Grev. 4. Abundant on mud in a drying ditch by the side of the Madingley Road, about 1 mile from Cambridge: Oct. 1898. 5. Between Swaffham Prior and the Beacon

Course, Newmarket Heath, on drying-up chalk mud: July, 1895; *W. West, Jun.*

Class **MYXOPHYCEÆ.**

Order Hormogoneæ.

Calothrix fusca (Kütz.) Born. & Flah. 3. Sheep's Green, Cambridge; Wimpole Park. In both instances the plants occurred either as solitary filaments or slightly gregarious, attached to *Vaucheria sessilis*. This is the first instance of this alga having been found in Britain, and its occurrence as an epiphyte on *Vaucheria* is rather remarkable, as it is usually found on such algæ as *Batrachospermum*, *Chætophora*, etc., which possess a more gelatinous thallus.

C. epiphytica West & G. S. West. 8. Guyhirn, on *Vaucheria dichotoma*. A much smaller species than the preceding, and only previously observed from West Africa.

Rivularia dura Roth. 5. Wicken Fen: very abundant in pools and peaty ditches, Aug. 1898. Forming olive- or dark-green hemispherical masses of small size, attached to *Myriophyllum spicatum* and *Chara hispida*.

R. minutula (Kütz.) Born. & Flah. 5. Chippenham Fen. This species was attached to the submerged portions of *Phragmites communis*, forming little pulvinate masses of a bright blue-green colour. Although this interesting species has not been previously recorded for England, it has a wide distribution on the continent, and may probably have been overlooked in this country.

Gloeotrichia Pisum (Ag.) Thur. 8. Twenty-foot River, between March and Guyhirn: very scarce, July, 1898.

Fam. Sirosiphoniaceæ.

Stigonema ocellatum (Dillw.) Thur. 5. Chippenham Fen, among *Utricularia vulgaris*.

Fam. Scytonemaceæ.

Tolypothrix lanata (Desv.) Wartm. [*T. coactilis* Kütz.; *T. ægagropila* (Kütz.) Rabenh.] 5. Wicken Fen, on the leaves of *Nymphæa alba*. 7. In large quantity in a pond about two miles S. of March. 8. Twenty-foot River, between March and Guyhirn.

T. tenuis Kütz. [*T. pygmæa* Kütz.] 5. Chippenham Fen, forming thick, felted, gelatinous masses among *Utricularia vulgaris*.

Nostoc microscopicum Carm. 3. Sheep's Green, Cambridge. 5. Chippenham Fen.

Anabæna variabilis Kütz. 3. Sheep's Green, Cambridge.

A. inæqualis (Kütz.) Born. & Flah. 6. Sutton, in ponds. 6. Guyhirn, in ponds.

Nodularia sphærocarpa Born. & Flah. 6. In ditches near Ely: July, 1898. The filaments possessed an excessively thin hyaline sheath, and the spores were noticed 3—11-seriate. *Distrib.*—France, Belgium, Italy.

Cylindrospermum stagnale (Kütz.) Born. & Flah. 5. Chippenham Fen, in peaty pools; Wicken Fen, in peaty ditches. 7. March, in ponds.

Lyngbya major Menegh., *L. ærugineo-cærulea* (Kütz.) Gom., and *L. ochracea* (Kütz.) Thur.

Phormidium molle (Kg.) Gom., *P. luridum* (Kg.) Gom., *P. valderianum* (Delp.) Gom., *P. laminosum* (Ag.) Gom., *P. tenue* (Menegh.) Gom., *P. angustissimum* W. & G. S. West, *P. inundatum* Kutz., *P. Retzii* (Ag.) Gom., and *P. autumnale* (Ag.) Gom. (inclus. *P. uncinatum*).

Oscillatoria princeps Vauch., *O. limosa* Ag., *O. ornata* Kütz., *O. irrigua* Kütz., *O. simplicissima* Gom., *O. tenuis* Ag., *O. amphibia* Ag., and *O. splendida* Grev.

O. decolorata G. S. West. 5. In ditch parallel to Burwell Lode: Aug. 1898. A curious and apparently saprophytic species of *Oscillatoria*.

O. proboscidea Gomont. 5. In a ditch parallel to Burwell Lode. Not previously recorded from Europe.

O. acuminata Gomont. 3. Sheep's Green, Cambridge. This striking species was obtained only once, in July, 1898. It has previously been seen only from Italy.

Spirulina major Kütz. [*S. oscillarioides* Kütz.] Crass. trich. 1·8 μ. 5. Wicken Fen.

Order Coccogoneæ.

Chamæsiphon incrustans Grun. [*Sphærogonium incrustans* (Grun.) Rostaf.] 3. Sheep's Green, Cambridge, on *Vaucheria* sp. and *Œdogonium* sp. 8. Twenty-foot River, between March and Guyhirn, on *Œdogonium crassiusculum* and var. *idioandrosporum*.

Glœochæte Wittrockiana Lagerh. [*Schrammia barbata* Dangeard 1889.] 2. Dernford Fen, 1 mile S. of Shelford. 3. Sheep's Green, Cambridge.

The cell-contents of this plant are most brilliant blue-green in colour, and very granulose; they are the contents of a typical Chroococcaceous alga. The bristles are excessively thin, 190—260 μ in length, and are attenuated to a very fine apex, near which minute branches or spurs are occasionally developed.

Glœothece confluens Näg. 2. Dernford Fen, 1 mile S. of Shelford. 5. Chippenham Fen.

Aphanothece microscopica Näg. 5. Chippenham Fen.

Synechococcus major Schröter. [*S. crassus* Arch.] 5. Chippenham Fen; Wicken Fen.

S. roseo-purpureus G. S. West. 5. Wicken Fen, in ditches, among *Mougeotia* sp.

This occurred in immense numbers in several ditches at the margins of Wicken Fen; it has characteristically short cells, is rarely much longer than broad, and is of a marked rose-purple colour, the few large granules in each cell being dark and conspicuous.

Glaucocystis Nostochinearum Itzigsh. 6. Roswell Pits, Ely.

Merismopedia hyalina Kütz. 6. Roswell Pits, Ely.

M. violacea (Bréb.) Kütz. 5. Wicken Fen.

M. glauca (Ehrenb.) Näg. 3. Trumpington; Lord's Bridge; Wimpole Park. 5. Wicken Fen. 7. Ponds S. of March. 8. Twenty-foot River, between March and Guyhirn.

M. punctata Meyen. 8. Guyhirn, in ponds.

M. elegans A. Braun. 5. Wicken Fen. Diam. cell. 6·5—9·5 μ. This fine species, much the largest of the genus, has only previously been met with from a few localities in Germany. The cells are somewhat angular by compression, and are of a brilliant blue-green colour. The families attain a very large size, and contain more numerous cells than those of any other species of *Merismopedia*; those observed were composed of 544—1856 cells, and reached a diameter of over 220 μ.

Tetrapedia glaucescens (Wittr.) Boldt. 2. Dernford Fen, 1 mile S. of Shelford. 6. Roswell Pits, Ely. Sutton West Fen.

Gomphosphæria aponina Kütz. 5. Chippenham Fen; Wicken Fen.

Microcystis roseo-persicinus (Kütz.) ——. [= *Clathrocystis roseo-persicinus* (Kütz.) Cohn.]

M. marginata (Menegh.). 3. Sheep's Green, Cambridge.

M. elabens Bréb. 5. Wicken Fen. 7. In ditches, March.

Porphyridium cruentum (Ag.) Näg. 1. Wall of the Senate House, and by the Leys School, Cambridge. 3. Newnham Mill, Cambridge.

Chroococcus turgidus (Kütz.) Näg. 5. Wicken Fen; Chippenham Fen.

Chroococcus macrococcus Rabenh. [= *Urococcus insignis* (Hass.) Kütz.] 5. Chippenham Fen.

C. pallidus Näg. 5. Chippenham Fen.

C. rufescens (Bréb.) Näg. 5. Chippenham Fen. 7. Ponds S. of March.

C. minor (Kütz.) Näg. 5. Wicken Fen. 6. Roswell Pits, Ely.

Class **BACILLARIEÆ.**

Order Centricæ.

Melosira varians Ag.

Cyclotella Kützingiana Chauvin, *C. Meneghiniana* Kütz., and *C. operculata* Kütz.

Coscinodiscus lacustris W. Sm. 8. Wisbech [*W. Smith*].

Order Pennatæ.

Amphora ovalis Kutz. and var. *Pediculus* Kütz.

Cocconema Ehrenbergii (Kütz.), *C. cuspidatum* (Kütz.), *C. affine* (Kütz.), *C. delicatulum* (Kütz.), *C. læve* (Näg.), *C. gastroides* (Kütz.), *C. lanceolatum* Ehrenb., *C. cymbiforme* (Kütz.) Ehrenb. and var. *parva* (W. Sm.), *C. Cistula* Hempr., *C. turgidum* (Greg.), and *C. cæspitosum* (Kütz.).

Mastogloia lanceolata Thw., *M. exigua* Lewis, and *M. Dansei* Thw.

Stauroneis Phœnicenteron (Nitzsch) Ehrenb., *S. anceps* Ehrenb. and var. *amphicephala* (Kütz.) V. H., and *S. Legumen* Ehrenb.

Navicula nobilis (Ehrenb.) Kütz., *N. major* Kütz., *N. viridis* Kütz., *N. borealis* Ehrenb., *N. divergens* (W. Sm.) Ralfs, *N. Brébissonii* Kütz., *N. subcapitata* Greg., *N. appendiculata* Kütz., *N. mesolepta* Ehrenb., *N. oblonga* Kütz., *N. peregrina* (Ehrenb.) Kütz. and var. *Menisculus* Schum., *N. gracilis* Kütz. and var. *neglectum* (Thwaites) G. S. West, *N. viridula* Kütz., *N. radiosa* Kütz. and var. *acuta* (W. Sm.) V. H., *N. cryptocephala* Kütz. and var. *veneta* (Kütz.) V. H., *N. rhynchocephala* Kütz. and var. *amphiceros* V. H., *N. Humilis* Donk., *N. lanceolata* Kütz., *N. Gastrum* (Ehrenb.) Donk., *N. tumida* W. Sm., *N. dicephala* Ehrenb., *N. elliptica* Kütz., *N. Tuscula* Ehrenb., *N. pusilla* W. Sm., *N. cuspidata* Kütz., *N. ambigua* Ehrenb., *N. sphærophora* Kütz., *N. exilis* Kütz., *N. Amphisbæna* Bory, *N. limosa* Kutz. and var. *gibberula* (Kütz.) V. H., *N. Iridis* Ehrenb. and vars. *amphigomphus*, *amphirhyncus*, and *affinis*, *N. Pupula* Kütz., *N. atomoides* Grun., and *N. Gallica* (W. Sm.) V. H.

Vanheurckia rhomboides (Ehrenb.) Bréb. var. *saxonica* (Rabenh.) G. S. West.

Amphipleura pellucida Kütz.

Gyrosigma attenuatum (Kütz.), *G. acuminatum* (Kütz.), *G. Spencerii* (Quekett), *G. Parkerii* (Harrison).

Amphiprora paludosa W. Sm. and *A. ornata* Bailey.

Gomphonema constrictum Ehrenb. and var. *capitatum* (Ehrenb.) V. H., *G. acuminatum* Ehrenb., *G. Augur* Ehrenb., *G. tenellum* Kütz., *G. parvulum* Kütz. and var. *subcapitata* V. H., *G. intricatum* Kütz. and var. *Vibrio* (Ehrenb.) V. H., *G. angustatum* Kütz., *G. gracile* Ehrenb. and var. *dichotomum* (Kg.) V. H. and *G. olivaceum* (Lyngb.) Kütz.

Rhoicosphenia curvata (Kg.) Grun.

Achnanthidium flexellum (Kütz.) Bréb.

Achnanthes Hungarica Grun., *A. microcephala* (Kg.) Grun., *A. exilis* Kütz., *A. linearis* (W. Sm.) Grun., and *A. lanceolata* (Bréb.) Grun.

Cocconeis Pediculus Ehrenb. and *C. Placentula* Ehrenb.

Epithemia turgida (Ehrenb.) Kütz., *E. Sorex* Kütz., *E. gibba* Kg. and var. *ventricosa* (Kg.) V. H., *E. argus* (Ehr.) Kg. and var. *alpestris* (W. Sm.) Rabenh., and *E. gibberula* Kg.

Eunotia pectinalis (Dillw.) Rabenh., *E. lunaris* (Ehrenb.) Grun. and var. *bilunaris* (Ehr.) Grun., *E. biceps* (W. Sm.), and *E.* sp. Valve slightly arcuate, sides subparallel and minutely undulate, apices rounded, slightly subcapitate; striæ 10 in 10 μ; length 106—111 μ. 5. Wicken Fen, frequent. Figured in the "Alga-fl. Cambs." 1899, t. 396, f. 12, 13.

Synedra pulchella Kütz. and var. *minutissima* (W. Sm.), *S. Vaucheriæ* Kg., *S. Ulna* (Nitzsch) Ehrenb. and vars. *splendens* and *oxyrhynchus*, *S. Acus* (Kg.) Grun. and vars. *delicatissima* and *angustissima*, *S. capitata* Ehrenb., *S. radians* (Kg.) Grun., and *S. famelica* Kg.

Asterionella formosa Hass.

Fragilaria virescens Ralfs, *F. capucina* Desmaz., *F. construens*

(Ehr.) Grun. and var. *Venter* V. H., and *F. mutabilis* (W. Sm.) Grun.

Meridion circulare (Grev.) Ag. and var. *constrictum* (Ralfs) V. H.

Diatoma vulgare Bory, *D. elongatum* Ag., and *D. hiemale* (Lyngb.) Heib.

Denticula tenuis Kg.

Cymatopleura elliptica (Bréb.) W. Sm. and *C. Solea* (Bréb.) W. Sm.

Surirella biseriata Bréb., *S. linearis* W. Sm., *S. robusta* Ehrenb., and *S. ovalis* Bréb. and vars. *angusta*, *pinnata*, *minuta*, and *ovata*.

Campylodiscus hibernicus Ehrenb.

Hantzschia Amphioxys (Ehrenb.) Grun.

Nitzschia Tryblionella (Ehr.) Grun., *N. constricta* (Kg.) Ralfs, *N. acuminata* (W. Sm.) Grun., *N. circumsuta* (Bréb.) Grun., *N. commutata* Grun., *N. Denticula* Grun., *N. sinuata* (W. Sm.) Grun., *N. dissipata* (Kg.) Grun. and var. *media* V. H., *N. parvula* W. Sm., *N. sigmoidea* (Ehr.) W. Sm., *N. vermicularis* (Kg.) Grun., *N. curvula* (Ehrenb.) W. Sm., *N. obtusa* W. Sm. var. *nana* Grun., *N. linearis* (Ag.) W. Sm. and var. *tenuis* (W. Sm.) Grun., *N. subtilis* Grun. and var. *paleacea* Grun., *N. Palea* (Kg.) W. Sm. and var. *debilis* V. H., *N. amphibia* Grun., and *N. acicularis* (Kg.) W. Sm.

FUNGI.

By F. T. Brooks, M.A., Gonville and Caius College.

The Fungus flora of the county as at present known cannot be described as a rich one. This is due partly to the fact that few persons in recent years have systematically collected Fungi in the district. The paucity of woodland in the county has also an unfavourable influence upon the extent of the fungus flora; for, according to recent agricultural returns, Cambridgeshire, excluding London, is the most badly wooded county in England, only about one per cent. of its area being covered by woodland.

With the advance of that branch of Botany known as Ecology it is becoming clear that the distribution of many saprophytic fungi is limited to places where certain special food materials are available. As investigation proceeds it will probably be found that each type of wood and heath has its own characteristic fungus flora. The habitats of many fungi are already known to be sharply defined, e.g. *Amanita muscaria* is found only under Birch trees, *Russula emetica* only under Beech. The following types of wood are met with in the county: (1) the Ash-Oak-Hazel association situated on calcareous glacial clay as at Madingley, (2) the Oak-Birch wood with a "heathy" ground flora such as is found on the Lower Greensand near Gamlingay, (3) the Oak wood with a ground flora of *Pteris aquilina* and *Holcus mollis* also found on the Lower Greensand near Gamlingay, and (4) the Beech wood on Chalk. Of these types the one richest to the mycologist is that of the Oak-Birch wood with a "heathy" ground flora, while the poorest on the other hand is that of the Oak wood whose ground flora is principally Bracken (*Pteris aquilina*).

Of plant diseases caused by parasitic fungi one may mention as occurring in the county the Larch Canker (*Dasyscypha calycina* or *Peziza Willkommii*) and the American Gooseberry Mildew (*Sphaerotheca mors-uvae*) of which some ninety cases were recorded during the summer of 1908. Black Scab of potatoes (*Chrysophlyctis endobiotica*) has not yet been recorded*.

The literature in regard to the mycology of the county is

* One case of this disease has since been found in the county.

extremely sparse. Ray in his *Methodus Plantarum circa Cantabrigiam nascentium* published in 1620 mentions *Amanita*, *Boletus*, *Agaricus* and *Lycoperdon*, but of course these "genera" are not synonymous with those of the present day. Martyn in the *Plantæ Cantabrigienses* of 1763 gives a list of 6 genera and 16 species of fungi. Relhan in the *Flora Cantabrigiensis* of 1820 makes a fairly complete survey of the mycology of the district. He records 23 genera and 255 species including the lower fungi and the organisms now known as Myxomycetes.

The following is a list of the higher fungi which have been recently found in the county, the majority having been recorded during 1908. When the district has been searched more thoroughly this list will doubtless be very much extended. The nomenclature of Massee's *British Fungus Flora* has been followed for all groups except the Uredineæ, for which Plowright's monograph has been used.

Basidiomycetes.

Gasteromycetes.

Scleroderma vulgare Fr.
—— bovista Fr.
Lycoperdon pyriforme Schœff.
—— bovista Linn.
Geaster fimbriatus Fr.
Ithyphallus impudicus Fisch.

Hymenomycetes.

Hirneola auricula-judæ Berk.
Exidia glandulosa Fr.
Dacryomyces stillatus Nees.
Calocera viscosa Fr.
Clavaria abietina Schum.
—— crocea Pers.
Thelephora laciniata Pers.
Peniophora quercina Cooke.
Stereum hirsutum Fr.
—— sanguinolentum Fr.
—— rugosum Fr.
—— purpureum Pers.
Solenia anomala Fr.
Hydnum auriscalpium Linn.
Phlebia merismoides Fr.
Merulius lacrymans Fr.
Dædalea quercina Pers.
Poria vaporaria Fr.
Polystictus versicolor Fr.
Fomes ulmarius Fr.
—— igniarius Fr.
Fomes vegetus Fr.
—— annosus Fr.
—— ribis Fr.
Polyporus squamosus Fr.
—— giganteus Fr.
—— sulphureus Fr.
—— hispidus Fr.
—— betulinus Fr.
—— adustus Fr.
Boletus chrysenteron Fr.
—— subtomentosus Linn.
—— æstivalis Fr.
—— badius Linn.
—— granulatus Linn.
—— edulis Bull.
—— rubinus W. G. Smith.
—— rubiginosus Fr.
—— viscidus Linn.
—— scaber Fr.
Coprinus comatus Fr.
—— micaceus Fr.
—— domesticus Fr.
Psathyrella disseminata Pers.
Hypholoma fascicularis Huds.
Stropharia albo-cyanea Desm.
Agaricus campestris Linn.
—— arvensis Schæff.
Paxillus involutus Fr.
Cortinarius armeniacus Fr.

Cortinarius jubarinus Fr.
—— rigidus Fr.
Crepidotus epigæus Pers.
Inocybe obscura Pers.
—— perbrevis Weinm.
Pholiota squarrosa Müll.
Hygrophorus miniatus Fr.
—— conicus Fr.
—— ovinus Bull.
Clitocybe infundibuliformis Schæff.
—— geotropa Bull.
—— inversus Scop.
—— brumalis Fr.
Laccaria laccata Scop.
Lactarius turpis Fr.
—— blennius Fr.
—— quietus Fr.
—— glyciosmus Fr.
—— subdulcis Fr.
Russula cyanoxantha Schæff.
—— rubra Fr.
—— fœtens Fr.
—— emetica Fr.
—— Queletii Fr.
Mycena capillaris Fr.
—— rugosa Fr.
—— galericulata Scop.
Collybia radicata Relh.
—— velutipes Fr.
—— tenucella Pers.
—— muscigena Schum.
Marasmius oreades Fr.
Tricholoma gambosum Fr.
—— personatum Fr.
Amanita muscaria Fr.
—— strobiliformis Vitt.
—— nitida Fr.

Uredineæ.

Uromyces fabæ Pers.
—— geranii DC.
—— betæ Pers.
—— poæ Rabh.
—— alchemillæ Pers.
—— ficariæ Schum.
—— scillarum Grev.

Puccinia asparagi DC.
—— thesii Desv.
—— pulverulenta Grev.
—— violæ Schum.
—— menthæ Pers.
—— primulæ DC.
—— vincæ Del.
—— graminis Pers.
—— glumarum Schmidt.
—— coronata Corda.
—— rubigo-vera DC.
—— poarum Nielsen.
—— caricis Schum.
—— schœleriana Plow.
—— moliniæ Tul.
—— suavolens Mart.
—— taraxaci Plow.
—— polygoni Pers.
—— pruni Pers.
—— tragopogi Pers.
—— smyrnii Corda.
—— adoxæ DC.
—— malvacearum Mont.
Triphragmium ulmariæ Schum.
Phragmidium violaceum Schultz.
—— rubi Pers.
—— subcorticatum Schrank.
—— rubi-idæi Pers.
Gymnosporangium sabinæ Dicks.
Melampsora helioscopiæ Pers.
—— lini Pers.
—— populina Jacq.
Coleosporium senecionis Pers.
—— sonchi Pers.
—— euphrasiæ Schum.
—— campanulæ Pers.
Cronartium ribicolum Dietr.
Uredo symphyti DC.
Cæoma euonymi Gmelin.
—— mercurialis Pers.
Aecidium grossulariæ Gmelin.
—— bunii DC.
—— punctatum Pers.

Ustilagineæ.

Ustilago longissima Sow.
—— hypodytes Schlecht.
—— segetum Bull.
—— olivacea DC.
—— violacea Pers.
Tilletia tritici Bjerk.
Urocystis anemones Pers.
—— violæ Sow.
Doassansia sagittariæ Fckl.

Ascomycetes.

Ascomyces pruni B. & Br.
—— deformans Berk.
—— aureus Magnus.
—— turgidus Phil.
Gymnoascus Reesii Baran.
Rhytisma acerinum Fr.
Bulgaria polymorpha Wettstein.
Ascobolus furfuraceus Pers.
Helotium virgultorum Karst.
Sclerotinia Fuckeliana.
—— fructigena Rehm.
Lachnea scutellata Gillet.
Dasyscypha calycina Fckl.
—— Stevensoni Sacc.
Geopyxis coccinea Mass.
Humaria granulata Sacc.
Peziza vesiculosa Bull.
—— venosa Pers.
Otidea leporina Fuckel.
—— aurantia Mass.
Helvella crispa Fr.
Mitrophora semilibera Lév.
Morchella esculenta Pers.
Geoglossum glabrum Pers.
Erysiphe graminis DC.
Erysiphe Martii Lev.
—— communis Wallr.
—— lamprocarpa Wallr.
—— Umbelliferarum Lév.
Phyllactinia suffulta Reb.
Sphærotheca pannosa Wallr.
—— mors-uvae Schwein.
Podosphæra Oxyacanthæ DC.
Microsphæra Grossulariæ Lév.
Nectria cinnabarina Fr.
—— ditissima Fr.
Hypomyces rosellus Tul.
Polystigma rubrum Pers.
Epichloe typhina Pers.
Claviceps purpurea Tul.
Phyllachora Graminis Pers.
Chætomium globosum Kze.
Pleospora herbarum Pers.
Gnomonia erythrostoma Pers.
Hypoxylon fuscum Fr.
Daldinia concentrica Bolt.
Xylaria polymorpha Grev.
—— hypoxylon Grev.
Eutypella Prunastri Pers.

LICHENES.

By the Rev. P. G. M. Rhodes, M.A., Pembroke College.

A good deal of work has been done at the lichens of Cambridgeshire, although the only systematic lists available are those in the various editions of Relhan's *Flora Cantabrigiensis*, especially that of the fourth and most complete edition, date 1820. He appears to have worked the county carefully, and though the advance of science has rendered many of his records doubtful, yet the synonymy of others is clear; and they form an important part of the list below. The writer is greatly indebted to Mr A. R. Horwood, of the Corporation Museum, Leicester, for working out the synonymy of Relhan.

There are a considerable number of records from Cambridgeshire quoted in Leighton's *British Lichen Flora* (3rd ed., 1879), chiefly however on the authority of "Relhan." It is not clear whether Leighton had examined specimens of Relhan's collecting in these cases, or whether he was merely quoting Relhan's work: if the latter, he appears to have quoted him in a somewhat haphazard manner. There are also a few important new records in Leighton.

From about this time onwards the county lichen-flora was worked by Mr Larbalestier, of St John's College, who included many Cambridgeshire species in the *exsiccata* he produced. Many new and rare species are thus recorded for the county, though the commoner species are but scantily represented. The *exsiccata* quoted are Larbalestier's *Lichen Herbarium* and *Lichenes rariores circa Cantabrigiam lecti*, ed. Larbalestier. Of this latter only one fascicle (the first) is available at Cambridge, and may be seen in the Town Library.

A number of important records are obtained from Crombie's *Monograph of British Lichens* (1894), in which a list is given of all the specimens in the British Museum. The collectors and dates of the specimens are not given; but they appear to have come chiefly from Larbalestier.

As records for the commoner species were only to be found in Relhan, the writer during 1908—9 collected a number of specimens with a view to establishing the present occurrence of these lichens

in the county. The Rev. H. P. Reader has most kindly identified these specimens, with the result that many of Relhan's records have been confirmed, and some new species added. It is plain that there is still plenty of room for work at these plants, and it is probable that many available records have been overlooked.

The old chalk turf produces an interesting growth of Cladoniei and Collemacei, and the trees of the county produce most of the common, and a few rare, species. Saxicolous lichens are poorly represented in the following list, as owing to the total absence of hard rocks they are necessarily confined to such habitats as church-walls and gravestones, whence they cannot easily be detached for examination. Probably a few of Relhan's species are extinct; e.g. *Lecanora lentigera.*

Abbreviations used below are:

Rel. = Relham's Flora Cantabrigiensis, various edd.
Le. = Leighton's British Lichen-Flora.
Cr. = Crombie's British Lichens (vol. I.).
LLH. = Larbalestier, Lichen Herbarium.
LRC. = Larbalestier, Lichenes Rariores circa Cantabrigiam lecti.
Rs. = P. G. M. Rhodes.

Records apparently of more than 50 years' standing are italicised. Records of Relhan's given by Leighton are simply quoted as *Rel.* Records in Crombie, whatever their apparent origin, are considered as modern: when obviously from Larbalestier, they are given under the latter's name only.

Collema pulposum Ach.	*Rel.*
C. nigrescens Ach.	*Rel.*
C. fasciculare Ach.	*Rel.*
Collema cristatum Hoffm.	3 Rs.
Collemodium microphyllum Nyl.	LLH.
C. Schraderi Nyl.	3 Fleam Dyke Rs.
Leptogium lacerum Gray	Cr.
Calicium *curtiusculum Nyl.	Oakington LLH.
C. trachelium Ach.	*Rel.*
Coniocybe furfuracea Ach.	5 *Rel.*
Trachylia tympanella Fr.	*Rel.*
Bæomyces rufus DC.	*Rel.*
B. roseus Per.	4 *Rel.*
Cladonia alcicornis Flörke	3 *Gogs Rel.*
C. pyxidata Fr.	*Rel.*, 3, 4, 6 Rs.
v. chlorophæa Flörk. f. lepidophora Flörke	3 Devil's Dyke Rs.
C. fimbriata Fr.	*Rel.*, 3 Cr., 4, 6 Rs.
C. furcata Hoffm.	3 *Rel.*
v. spinosa Hook.	3 *Gogs Rel.*, Cr.; Fleam Dyke, etc. Rs.

C. pungens Flörke	3, 6 Rs.
f. foliosa Flörke	3 Hildersham Rs.
C. coccifera Schaer.	*Rel.*
Cladina uncialis Nyl.	3 *Gogs Rel.*
Ramalina farinacea Ach.	*Rel.*, Cr., 1, 5, 6 Rs.
R. fraxinea Ach.	*Rel.*, 5 LRC., 6 Rs.
R. fastigiata Ach.	*Rel.*, 5 Cr., LRC., 3, 5, 6 Rs.
R. pollinaria Ach.?	1 Rs.
Usnea florida Ach.	*Rel.*
U. ceratina Ach. (= "plicata")	*Rel.*
Alectoria jubata Nyl.	*Rel.*, 4 Cr.
Cetraria aculeata Fr.	3 *Rel.*
Evernia prunastri Ach.	*Rel.*, Cr., 3, 5 Rs.; common.
Parmelia perlata Ach.	*Rel.*
P. saxatilis Ach.	*Rel.*, 3 Rs.?
P. sulcata Tayl.	2, 3, 4 Rs.
P. Borreri Tayl.	1, 3 Rs.
P. caperata Ach.	*Rel.*, 4? Cr., 5 Rs.
P. acetabulum Dub.	2 Rs.
P. exasperata Nyl.	1, 2, 3, 5 Rs.
P. subaurifera Nyl.	Wimpole Park LLH.
P. fuliginosa Nyl.	3?, 5 Rs.
P. physodes Ach. (f. labrosa)	*Rel.*, Cr., 4 Rs.
Stictina limbata Nyl.	G. Bentham, ap. Le.
Lobaria pulmonaria Hoffm.	4 *Rel.*
Solorina saccata Ach.	*Rel.*, ap. Le.
Peltigera canina Hoffm.?	*Rel.*, Cr., 6 Rs.
P. spuria Leight.	3 Cr.
P. polydactyla Hoffm.	*Rel.*, 3 Cr.
Physcia parietina De Not.	*Rel.*, LLH., LRC., 1, 2, 3, 6 Rs.
f. cinerascens Leight.	2, 3, 6 Rs.; frequent.
P. polycarpa Nyl.	3 LRC., LLH., Rs.
P. lychnea Nyl.	1 Trumpington Rs.
P. ciliaris DC.	*Rel.*, LLH.
P. pulverulenta Nyl.	*Rel.*, LRC., 1, 2 Rs., 5 Cr.
v. subvenusta Nyl.	Cr.
P. *pityrea Nyl.	*Rel.*, LLH., 2 Rs.
P. *tenella Nyl.	*Rel.*, 1, 3 Rs.
P. aipolia Nyl. v. cercidia Nyl.	LLH., LRC., 3 Rs.
P. cæsia Nyl.	1 Coe Fen Rs.
P. obscura Nyl.	In Cambridge LLH. [Near Newmarket LRC.]
P. ulothrix Nyl. v. virella Cr.	1 Rs., 3 LRC., Cr.

In Coe Fen (1) associated with *P. parietina*, and gives the purplish reaction with K.

P. adglutinata Nyl.	3 Rs., 4 LLH.
Lecanora hypnorum Ach.	3 *Rel.*
L. lentigera Ach.	3 *Gogs Rel.*, Cr.

L. saxicola Ach.	1 *Rel.*
L. murorum Ach.	1 Rs.
v. corticola Nyl.	Gt Wilbraham LLH.
L. *decipiens Nyl.	1 LLH.
L. callopisma Ach.	3 Quy Church LLH.
L. teicholyta Ach.	1 LLH., Cr.; frequent, Le.
L. laciniosa Nyl.	3 LLH., 6? LRC.
L. vitellina Ach.	*Rel.*, 2, 3 Rs.
L. medians Nyl.	1 LLH.
L. citrina Ach. f. corticola	Wimpole Park LLH.
L. aurantiaca Nyl.	*Rel.*
L. *hæmatites Nyl.	3 Cherry Hinton LRC. (and Le.). Bottisham LRC.
L. cerinella Nyl.	Near Cambridge Cr.
L. pyracea Nyl.	LLH.
L. luteoalba Nyl.	LLH., LRC.
L. phlogina Nyl.	LLH., LRC.
L. *calva Nyl.	3, 4 *Rel.*
L. colobina Ach.	Cr.
L. circinata Ach.	*Clare Bridge* etc. *Rel.*, Cr.
L. galactina Ach.	1 LRC., 1, 2 Rs.
L. subfusca Nyl.	*Rel.*?, LLH., 1, 3 Rs.
v. campestris Nyl.	1 Rs.
L. allophana Nyl.	2, 3, 5 Rs.
L. Parisiensis Nyl.	3 LLH., LRC.
L. rugosa Nyl.	3 Rs.
L. *chlarona Nyl.	LLH., LRC., 1, 3 Rs.
L. albella Ach.	LLR., 2 Rs.
L. angulosa Ach.	3 Rs.
L. crenulata Nyl.	1, 3 *Rel.*
L. Hageni Ach.	LLH., LRC.
L. sulphurea Ach.	*Rel.*, LLH.; 1 *Rel.*
L. varia Ach.	1, 3 Rs., 4 LLH.
L. symmictera Nyl.	4 LLH. (named L. symmicta).
var. aitema Nyl.	4 LLH.
L. atra Ach.	*Rel.*, LLH., Cr., 3 Rs. (corticolous).
L. calcarea Somn. var. Hoffmanni Som.?	Gogs *Rel.* (Lichen Hoffmanni).
L. parella Ach. v. Turneri Nyl.	5 *Rel.*
Pertusaria globulifera Nyl.	Cr.
P. amara Nyl.	*Rel.*, 3, 5 Rs.
P. communis DC.	*Rel.*, 5 Rs.
Urceolaria scruposa Ach.	*Sir J. E. Smith* ap. Le., LLH.; 3 *Rel.*, Cr.
U. *bryophila Nyl.	6 Rs.
Lecidea decipiens Ehrb.	3 *Rel.*
L. ostreata Hoffm.	*Rel.*
L. flexuosa Fries, var. æruginosa Boor.	1 or 3 LLH.

L. quernea Dicks.	5 *Rel.*
L. sanguinaria L.	*Rel.*
L. parasema Ach.	*Rel.*, 3 Rs.
L. coarctata Sm.	*Rel.*
L. fuscoatra Ach.	*Rel.*
L. canescens Dicks.	*Rel.*, 1, 2, 3, 4, 6 Rs., 5 LLH.
L. myriocarpa DC.	1, 2, 3, 6 Rs.
f. chloropolia Fr.	1 LLH., 1 LRC.
f. saprophila Ach.	3 ?, 4 LLH.
L. vesicularis (= cœruleonigricans) Lightf.	3 *Rel.*, Le. etc.; Rs.
L. Ehrhartiana Sch.	*Rel.*
[L. diluta Pers.	Near Newmarket. Qy in county?]
L. incompta Bor.	LLH.
L. alboatra Hoffm. var. epipolia Ach.	1 *Rel.*, 3 *Rel.*, LLH.
L. sabuletorum Flk.	LRC.
[f. minor Larbal.	Near Newmarket LLH.]
L. premnea Ach. corticola	Cheveley Park LLH.
L. rubella Ehrh.	Near Cambridge LLH.
L. muscorum Sw.	LRC.; 3 *Rel.*, 6 Rs.
L. truncigena Ach.	LLH.
Opegrapha atra Pers.	3 Rs.
O. Turneri Leight.	LLH.
O. vulgata Ach.	*Rel.*, LLH.
O. herpetica	Teversham Rs.
Anthonia Swartziana Ach.	3 Rs.
A. astroidea Ach.	LLH.
A. pruinosa Ach.	*Rel.*
Graphis scripta Ach.	*Rel.*
Endocarpon hepaticum Ach.	3 Rs., *Salwey.*
Verrucaria rupestris Schrad.	3 Rs.
V. nigrescens Pers.	6 Rs.
V. calciseda DC.	3 Rs.
V. gemmata Ach.	LLH.
V. nitida Weig.	*Rel.*
V. hymenogonia Nyl.	Newmarket Heath LLH.
V. Mortarii Arn.	3 Quy Churchyard, Larb. ap. Le.
Strigula Babingtonii Berk.	Cambridge, Bab. ap. Le.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

On the Nature and Velocity of an Ion in a Gas. By R. D. Kleeman, B.A., Emmanuel College, D.Sc. (Adelaide), Mackinnon Student of the Royal Society, and Clerk Maxwell Student of the University of Cambridge. (Communicated by Mr A. Wood.)

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It has usually been supposed in investigations on the nature and motion of an ion in a gas that its nature varies with the temperature but is constant at constant temperature, and formulae for the velocity of the ions have been obtained on these and additional suppositions. But it follows from thermodynamical and other considerations that the nature of the ion must be continually changing at constant temperature. The formation and breaking up of an ion cluster is governed by the same laws as those which govern the formation and dissociation of a molecule in a gas, the only difference is that in one case the cluster of atoms is held together by chemical attraction while in the other by chemical and electrical attraction, but the nature of the forces of attraction does not affect the general nature of the course of changes the cluster undergoes. We know that there is no perfectly stable chemical system, every molecule must sometime get dissociated, and therefore has a finite life. The process is regulated to a certain extent by the magnitude of the heat of formation of the molecule, the law of mass action, and the laws of thermodynamics. The association or dissociation products in a mass of matter may of course in some cases be comparatively small, but nevertheless the process of dissociation and association is continually going on. Thus for example in a mass of water vapour a number of molecules are dissociated every second into hydrogen

and oxygen molecules, and these again combine to form water molecules. But the mass of hydrogen and oxygen existing at any instant is at ordinary temperatures a very small fraction of the total mass of water vapour. When however the temperature is raised the amounts of the dissociation products are greatly increased. The same considerations apply to an ion in a gas; from which it follows that the extent of clustering of an ion is continually changing at constant temperature, and the same laws apply to the process as to the chemical association and dissociation in a gas.

It follows therefore that the formulae deduced for the velocity of an ion in a gas on the supposition that it is stable do not represent the facts, and it is therefore desirable to investigate the average velocity and other properties of an ion whose nature is continually changing.

Reasoning from the analogous case of chemical change the changes in the clustering of an ion may take place in the following way. When a free ion* in a gas collides with a molecule it may get attached to it, forming what we will call a cluster 1. When a cluster 1 collides with a molecule it may get broken up into its constituent simple ion and neutral molecule, or the molecule may get attached to the cluster forming a cluster 2. Similarly a cluster 2 on colliding with a molecule may form a cluster 3, or break up into a cluster 1 and a neutral molecule, or into the free ion and two neutral molecules, etc. Thus when a cluster of the nth kind collides with a molecule $n+1$ different things may happen.

In an ionised gas at a high pressure—say atmospheric pressure—the number of ions in comparison with the number of neutral molecules is usually extremely small, and the number of collisions of the ion clusters with one another is therefore very small in comparison with the number of collisions with neutral molecules, and need not therefore be taken into account. When however the gas is at a very low pressure as in a discharge tube, the collisions between the clusters become of importance. In that case we might get clusters formed as a result of a collision having two or more free ions as nuclei.

In formulating an expression for the velocity of an ion in a gas in an electric field we must therefore take into account that its nature is continually changing. We will now endeavour to obtain such an expression. Let t_0 denote the average life of a free ion in the gas under consideration, t_1 that of a cluster 1, t_2 that of a cluster 2, and so on. Let v_0 denote the velocity of the free ion,

* A free ion is an electrically charged particle without any molecules attached to it; in the case of the negative ion it is the electron.

v_1 that of a cluster 1, and so on. The average velocity V of the ion—the quantity usually measured—is then given by

$$V = v_0 t_0 u_0 + v_1 t_1 u_1 + v_2 t_2 u_2 + \ldots \text{ or } V = \sum_0^n v_n t_n u_n,$$

where u_0 denotes the number of times per second the ion is in the free state, and u_1 the number of times it forms a cluster 1, etc., and $1 = t_0 u_0 + t_1 u_1 + \ldots$.

The life of a cluster varies inversely as the pressure. Thus if the pressure be doubled, the number of collisions of each cluster with the neutral molecules is doubled, and its chance of breaking up consequently doubled, and the life of each cluster is thus halved. It will be observed that therefore the relative values of t, the relative lives of the clusters, are independent of the pressure of the gas.

The life of a cluster is obviously inversely proportional to its velocity, and therefore inversely proportional to the square root of the temperature. But its life must be affected by the temperature in an additional way. The collisions of the clusters with the molecules become more violent with rise of temperature, and thus the liability of a cluster to get broken up during a collision is increased. Further a rise of temperature probably affects the chances of a change in the nature of the clustering of the various clusters in a different degree.

The values of u_n are proportional to the pressure, for if the pressure be increased n times the time of a cycle of clustering through which the ion passes is $\frac{1}{n}$ of the previous value, and therefore it passes n times oftener in a given time through the cycle than previously. It follows therefore that at constant temperature $t_n u_n$ is independent of the pressure. Along the same line of reasoning it can be shown that u_n is proportional to the velocity of the cluster and therefore proportional to the square root of its temperature. But u_n is affected in addition to this by the temperature in a similar way to the life of an ion.

The velocity v of a stable ion depends on the pressure; from the kinetic theory of gases we would expect it to vary inversely as the pressure. We would also expect it to be independent of the temperature provided the density is kept constant. The average velocity V should thus according to the above equation vary inversely as the pressure. But this will hold only under certain conditions which will be discussed later.

Let us now consider the special case in which clusters 1 only are formed to any appreciable extent in the gas. Suppose n_0 free ions are converted per second into clusters 1; n_0 clusters 1 will

then be converted per second into free ions. The concentrations c_0, and c_1 of the free ions and clusters respectively are therefore given by $t_0 n_0 = c_0$, $t_1 n_0 = c_1$. The truth of these equations will at once appear from the following considerations. Suppose no clusters 1 exist at the beginning of the transformation of free ions into clusters 1. After a time t_1, the clusters 1 will begin to be transformed into free ions at the same rate; equilibrium of the concentration is then reached, being given by $t_1 n_1 = c_1$. Similarly the other equation can be established. Consider an ion passing through a cycle of clustering. It will be evident that u_n, the number of times an ion becomes a cluster n per second, is proportional to n_n, the number of clusters forming or breaking up per second, or $u_n = n_n a$. Since $1 = t_0 u_0 + t_1 u_1$ we have

$$1 = a(t_0 n_0 + t_1 n_1) = a(c_0 + c_1)$$

or

$$a = \frac{1}{c_0 + c_1}.$$

The equation for the average velocity of the ion may then be written

$$V = (c_0 v_0 + c_1 v_1)\frac{1}{c_0 + c_1} = \left(v_0 + \frac{c_1 v_1}{c_0}\right)\frac{1}{1 + \frac{c_1}{c_0}}.$$

It can be transformed into one free from the ratio $\frac{c_1}{c_0}$. Van 't Hoff has deduced the equation

$$\frac{d}{dT}\left(\log \frac{c_1}{c_0}\right) = \frac{H_1}{T^2},$$

where c_0 and c_1 are the concentrations at the temperature T of two different systems obeying the law of mass action, and H_1 is the heat of transformation or change in potential energy in calories per gram molecule of either of the constituent systems when the system 2 changes into system 1.

This equation reduces the previous equation into the form

$$V = \left(v_0 + v_1 A_1 e^{-\int \frac{H_1}{T^2} dT}\right) \frac{1}{1 + A_1 e^{-\int \frac{H_1}{T^2} dT}},$$

where A_1 is a constant depending only on the nature of the cluster. This equation shows how the velocity of the ion in a gas whose density is kept constant depends on the temperature.

The quantity H_1—the energy necessary to move the simple ion or electron from the cluster to infinity—may be a function of T the temperature. But it will probably vary little with the

temperature. Supposing it not a function of T the above equation becomes

$$V = \left(v_0 e^{\frac{H_1}{T}} + v_1 A_1\right) \frac{1}{A_1 + e^{\frac{H_1}{T}}}.$$

A superior limit of the value of H_1 can be obtained. The energy necessary to move an ion away from a cluster to infinity we may take for granted cannot be greater than the energy to make a pair of ions, viz. about 3×10^{-11} ergs. Since there are about $\frac{1}{2 \times 1{\cdot}61 \times 10^{-24}} = 3{\cdot}12 \times 10^{23}$ molecules of hydrogen in one gram molecule, the value of H_1 must be less than

$$\frac{3{\cdot}12 \times 10^{23} \times 3 \times 10^{-11}}{4{\cdot}2 \times 10^{7}} = 2{\cdot}4 \times 10^{5} \text{ cal.}$$

It is however probably of the same order. It should be observed that the value of H_1 increases with the size of the atom or molecule to which the electron is attached.

Let us next consider the velocity of an ion in a gas when any number of different kinds of clusters can be formed. It can be easily proved that in general $t_n n_n = c_n$, where t_n denotes the life of a cluster of the order n, c_n the concentration of the clusters per c.c., and n_n the number undergoing a change per second. Since n_n clusters change per second one cluster will change during the time $\frac{1}{n_n}$. Since each of the clusters changing has existed as a cluster n for a time t_n, there must be $t_n \Big/ \frac{1}{n_n}$ clusters per c.c. to provide for a change of one cluster during the time $\frac{1}{n_n}$, and this is the concentration c_n, or $c_n = t_n n_n$. We have then

$$V = v_0 t_0 u_0 + v_1 t_1 u_1 + v_2 t_2 u_2 + \ldots,$$

where $$t_0 n_0 = c_0, \quad t_1 n_1 = c_1, \quad t_2 n_2 = c_2, \text{ etc.,}$$

where n_0 denotes the number of free ions changing into clusters per second, and n_1 the number of clusters 1 changing into other clusters and free ions per second, and n_2 the number of clusters 2 changing into other clusters and free ions per second, and so on. We have further $u_0 = a n_0$, $u_1 = a n_1$, etc., and

$$1 = t_0 u_0 + t_1 u_1 + \ldots = a\,(t_0 n_0 + t_1 n_1 + \ldots) = a\,(c_0 + c_1 + \ldots).$$

The above general equation for the velocity now becomes

$$V = \left(v_0 + v_1 \frac{c_1}{c_0} + v_2 \frac{c_2}{c_0} + \ldots\right) \frac{1}{1 + \frac{c_1}{c_0} + \frac{c_2}{c_0} + \ldots}.$$

This equation may be transformed in a similar way as before, and we have

$$V = \frac{\left(v_0 + v_1 A_1 e^{\int \frac{H_1}{T^2}.dT} + v_2 A_2 e^{\int \frac{H_2}{T^2}.dT} + \ldots\right)}{1 + A_1 e^{\int \frac{H_1}{T^2}.dT} + A_2 e^{\int \frac{H_2}{T^2}.dT} + \ldots},$$

where H_1 denotes the energy of formation of a cluster 1 from a free ion and a neutral molecule, H_2 the energy of formation of a cluster 2 from a free ion and two neutral molecules, and so on, and A_1, A_2, ..., are constants. The variation of the velocity with temperature depends thus on the variation of the quantities

$$\int \frac{H_1}{T^2}, \quad \int \frac{H_2}{T^2}, \ldots,$$

with the temperature.

It is of interest next to find a relation, should such exist, between the quantities n_0, n_1, ... Let us first consider the special case in which a cluster can only form a cluster of the next higher order or become a free ion. The free ion can only change into cluster 1, and therefore $n_0 = n_1$. Let the fraction α_1 of the number of clusters 1 changing per second, be converted into clusters 2, the rest being then converted into free ions. Therefore $n_2 = \alpha_1 n_0$. The fraction α_1 depends on the average nature of the collision of a cluster 1, which depends on the nature of the cluster and surrounding molecules and their temperature. It does not seem possible to express α_1 in a simple way in terms of these quantities. Of the number of clusters 2 that change per second, let $\alpha_2(\alpha_1 n)$ be converted into clusters 3, where α_2 is a fraction, the rest being converted into free ions and clusters 2. Thus $n_3 = \alpha_2 \alpha_1 n_0$; and generally we have

$$n_m = \alpha_{m-1} \alpha_{m-2} \ldots \alpha_1 n_0,$$

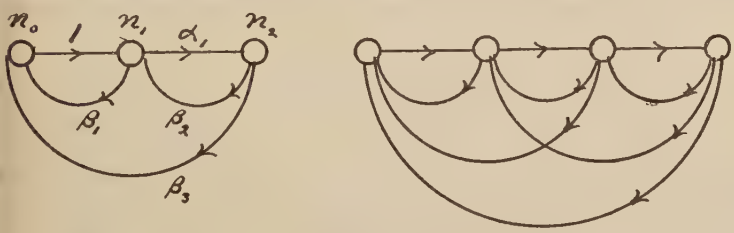
where n_m denotes the number of clusters of the mth order changing per second into other clusters. Since $\alpha_1, \alpha_2, \ldots$, can only be fractions, the value of n_m decreases with an increase of the value of m. The equations for the concentrations of the clusters thus become

$$t_0 n_0 = c_0, \quad t_1 n_0 = c_1, \quad t_2 \alpha_1 n_0 = c_2, \quad t_3 \alpha_2 \alpha_1 n_0 = c_3, \text{ etc.}$$

Thus we see that if the life of each kind of cluster were the same, the concentrations of the various clusters in the gas would decrease with their complexity. But the more complex the cluster the greater is its liability to get broken up on collision and consequently the shorter is its life. In general then the concentrations c_0, c_1, $c_2 \ldots$, would decrease very rapidly in magnitude in a gas.

Further, the more violent the collision of a cluster with a molecule the less becomes the chance of a cluster of a higher order being formed. Therefore the higher the temperature the more rapidly the fractions α_1, α_2, ..., will decrease relatively to one another. A temperature therefore exists at which there are comparatively few clusters, and we are then practically dealing with the simple ion. Such a state is reached by the ions in a flame, as indicated by the enormously greater velocity of the negative ion in a flame, than that obtained at ordinary temperatures in air.

Let us next consider the general case in which the cluster may change into one of the next higher order, or into any cluster of a lower order or free ion. The process of change of the various clusters into one another is indicated for two cases by diagrams,



In one case the cluster of greatest complexibility is 2 and in the other 3. It follows directly from the diagrams that in all cases n_0 free ions are converted per second into clusters 1. The number of clusters 1 changing per second must be equal to the number forming, and n_1 is therefore equal to n_0 plus the number of clusters of higher order transformed per second into clusters 1. Thus we see that in general $n_1 > n_0$. It will also be evident from the diagrams that n_n, the change per second per c.c. of the clusters of greatest complexibility, must be a fraction of n_{n-1}, or in general $n_{n-1} > n_n$.

Let us apply this result to the special case in which only clusters of the first and second order are supposed to be formed. We have then $n_0 < n_1 > n_2$. Therefore if the lives of a free ion and a cluster 1 and 2 are equal to one another, it follows from the equations connecting t_m, n_m, and c_m, that the concentrations of the clusters 1 is greater than that of the free ions or clusters 2. But the life of a cluster 1 is probably greater than that of a free ion, for we would expect it to be easier for a free ion to attach itself to a molecule on colliding with it, than a cluster 1 to attach itself, or get broken up into the free ion and neutral molecule. Its life is also probably greater than that of a cluster 2, because we have assumed that a cluster 2 is saturated with molecules, and is therefore more liable to get broken up on collision than a cluster 1. The concentration of the clusters 1 may therefore be

much greater than that of the clusters 2 and that of the free ions. The average velocity of the ion may in this case therefore be approximately that of the cluster 1.

It will be of interest to express n_1 and n_2 in terms of n_0 and the fractions expressing the proportions in which n_n clusters n change per second into other different clusters. Suppose $\alpha_1 n_1$ of the clusters 1 changing per second are converted into clusters 2, and $\beta_1 n_1$ converted into free ions, and suppose $n_2\beta_2$ of the clusters 2 changing are converted into clusters 1 and $n_2\beta_3$ into free ions. n_0 free ions per second will always be converted into clusters 1. The number of clusters changing per second is equal to the number being formed, which gives one equation on considering the free ions, and two equations for every cluster. The equations in the case under consideration are

$$n_0 = n_1\beta_1 + n_2\beta_3, \quad n_1 = n_0 + n_2\beta_2, \quad n_1 = n_1\alpha_1 + n_1\beta_1,$$
$$n_2 = n_1\alpha_1, \qquad\qquad n_2 = n_2\beta_2 + n_2\beta_3,$$

from which we obtain $n_1 = \dfrac{n_0}{1-\beta_2\alpha_1}$, and $n_2 = \dfrac{n_0\alpha_1}{1-\beta_2\alpha_1}$. Since α_1 is a fraction we have $n_0 < n_1 > n_2$, a result we obtained in a general way before. The equations in the case when the cluster of greatest complexibility is greater than 3 can be easily obtained in the same way, but possess no special interest.

Since the velocity of translation of a molecule increases with the temperature the probability of a cluster getting broken up on collision increases with rise of temperature. The values of the αs thus decrease and those of the βs increase with increase of temperature. A study of the diagrams then shows that the value of n_m for a cluster m must in general decrease with rise of temperature. And since the value of t_m also decreases under these circumstances, the value of c_m rapidly decreases with rise of temperature. The average velocity should thus in general increase with rise of temperature.

The larger the cluster round an ion the less will its mass depend on that of its nuclei. The clustering will thus have the effect of making the average velocity of ions having different nuclei lie nearer to one another in value than the velocities of the simple ions.

If $v_0 = v_1 = v_2 = \ldots$, that is if the velocity of a stable system through a gas is independent of the mass of the system, it follows from the above equation that the average velocity is independent of the temperature. But since it has been found that the velocity depends considerably on the temperature, the velocity of a stable system must depend both on its own mass and on that of a molecule of the surrounding gas. This would also follow from considerations based upon the kinetic theory of gases.

A sudden change in velocity of an ion with increase of temperature would indicate a sudden change in the values of

$$H_1, H_2 \ldots, \text{ or } \alpha_1, \alpha_2, \ldots .$$

The quantities H_m, α_m, will change simultaneously, they will in fact increase or decrease simultaneously, since the former denotes the energy necessary to break up the cluster m and the latter its chance of not getting broken up during a collision but forming a cluster of a higher order. Now H. A. Wilson* found that the velocity of the ions in a flame changes very suddenly at a certain temperature as the temperature of the flame is increased. It follows therefore that the forces which hold a cluster together may undergo very sudden changes with the temperature. These forces probably consist of the attraction due to electric induction and the chemical attraction between the molecules. This point is of special interest in connection with the effect of temperature of chemical attraction. The writer has investigated this subject† and obtained some evidence that the chemical attraction of a molecule depends on its temperature.

If the velocity v of a stable ion varies inversely as the pressure the average velocity given by the above equation will also vary inversely as the pressure. But this will only hold if the distance over which the velocity is measured is greater than $(t_0v_0 + t_1v_1 + \ldots)$ or $\Sigma_0^m t_m v_m$, supposing the ions begin their journey as simple ions. When the distance is less than that, the clusters of higher order will have less chance of forming than those of lower, for a cluster 1 can only be formed after a time t_0 during which the ion has moved over a distance t_0v_0, and a cluster 2 can only be formed after a time $(t_0 + t_1)$ during which the ion has moved over a distance $(t_0v_0 + t_1v_1)$, etc. The average velocity will thus be greater than that under normal conditions, since the velocity of a cluster increases with decrease of complexity. Experiments have shown that the velocity of the negative and positive ion varies inversely as the pressure of the gas down to a pressure of a few mm. of mercury, below this pressure the velocity of the ion increases more rapidly than that given by this law. Since the velocity of the simple clusters of the negative ion very likely have a greater velocity than those of the positive ion, the deviation of the average velocity of the negative ion from varying inversely as the pressure will be larger than in the case of the negative ion, and this has been found to be the case. The pressure at which the inverse pressure law for the velocity begins to break down is of interest and importance, for we then have $d = \Sigma_0^m t_m v_m$, where d is the distance over which the velocity is measured. The life t

* *Phil. Trans. Roy. Soc.* A, 1909, Vol. CXCVII. (1901).
† *Phil. Mag.* January, 1911, pp. 93, 94.

of an ion is inversely proportional to the pressure of the gas, and so is very probably the velocity v of a stable ion, therefore d from the above equation is inversely proportional to the square of the pressure. It decreases therefore very rapidly with increase of pressure. An interesting set of experiments could be carried out on the value of d for different gases.

The change in the clustering that the ions in a gas undergo produces under certain conditions a lagging effect in the motion of some of the ions. Thus if a number of ions are made at the same instant at a point in a gas under an electric field they will not arrive simultaneously at another point along their path. The ions begin their life as free ions, but arrive at the second point as free ions and clusters of various orders, and hence will have taken different times to travel over the distance between the two points. When a number of ions in a gas begin their life as free ions the time taken for the concentrations of the various clusters to become constant is theoretically infinite: in practice, however very approximate constancy of the concentrations is probably reached in a very short time. If the ions are under the action of an electric field when they are produced the concentrations of the clusters at a distance ud from the point from which they begin their motion are independent of the pressure of the gas, where u is any given constant. The quantity d, it will be remembered, is the minimum distance in a gas within which each kind of cluster has a chance of being formed and depends on the pressure. It follows therefore that the distance from the starting point of the ions within which the concentrations of the various clusters becomes practically constant, decreases with decrease of d. When this distance is small in comparison with the distance over which the velocity is measured there is little lagging of ions. It is therefore at low pressures only, when d is comparatively not very small, that this effect becomes appreciable. This result is of interest in connection with measurements of the velocity of ions in which an alternating electric field is used. If the ions are stable the region they traverse under the field is sharply defined, and does not change with time. If, however, the clusters are continually changing in magnitude the region traversed is not sharply defined. Each ion does not necessarily go through the same cycle of clustering, thus a cluster 2 on colliding with a molecule may become a cluster 3, or a simple ion, or a cluster 1, and thus the average velocity of each ion is not the same. But the maximum difference in velocity that can exist between two ions will only become appreciable in magnitude at low pressures. The effect of this would be to make the velocity apparently increase with decrease of pressure, as the velocity of the quickest moving ion is actually measured, and this is what has been observed. This

xperimental result is thus evidence of the unstable nature of the ons in a gas.

When the pressure of a gas is low and the ions are under the influence of an electric field, the formation and breaking up of the clusters may possibly be affected by the field. This would certainly be the case when the velocity given to a cluster by the field is comparable with the velocity of translation of a molecule, for this would have the effect of greatly increasing the violence of a collision and causing that fewer clusters of high complexibility are formed. The field may also have the effect of completing the partial separation of the simple ion in a cluster from its associated molecules during a collision of the cluster. If such an effect exists the average velocity of an ion for unit intensity of electric field should depend on the intensity of the field used. The experiments that have been carried out on the velocity of ions show incidentally that it is independent of the intensity of the electric field over the range of fields used. But it is very likely that this does not hold for fields of great intensity, with which experiments have not yet been carried out.

We will now endeavour to find an expression for v, the velocity of a stable system in a gas. A number of formulae have been developed on the assumption that a collision wipes out the previous history of an ion. But this assumption is far from representing the actual facts. This will appear at once from considering the motion of a heavy molecule in a light gas. The moving molecule will never be brought to rest by a collision in this case, the effect of the surrounding molecules being to reduce its velocity intermittently.

But it is difficult to formulate an expression for the velocity, because we know so little about the real nature of a collision. Perhaps the most trustworthy expression is obtained by combining Townsend's equation for the diffusion of ions with Maxwell's equation for the diffusion of one gas into another as Sir J. J. Thomson has done*. Townsend's equation is $V = \frac{DNe}{p}$, where V denotes the velocity of an ion and D its coefficient of diffusion, N denotes the number of molecules per c.c. and p their pressure, and e the charge of an ion. Maxwell regarded the molecules simply as centres of force, and supposed the force between two molecules to be given by $\frac{B}{z^5}$, where B is a constant depending on the nature of the molecules and z is their distance of separation. This law led to the equation

* *Camb. Phil. Soc.* Vol. xv. Pt 4, p. 375.

$$D = \frac{p_1}{\rho_1 \rho_2} \frac{p_2}{A\left\{\frac{B}{(m_1 m_2 (m_1 + m_2)}\right\}^{\frac{1}{2}}} \frac{1}{p},$$

where D denotes the coefficient of diffusion of a gas 1 into a gas 2 whose partial pressures are p_1 and p_2, and densities ρ_1 and ρ_2, and $p = p_1 + p_2$, m_1 and m_2 denote the molecular weights of the gases and A a constant. When the number of molecules 1 is small in comparison with the number of molecules 2 we have $p = p_2$. Writing $\frac{p_1}{\rho_1} = \frac{RT}{m_1}$ and $\rho_2 = \frac{p_2 m_2}{RT}$ and combining the equations we obtain

$$V = \frac{e}{A} \frac{RT}{p_2 m_1 m_2} \frac{1}{\left\{\frac{B}{(m_1 m_2 (m_1 + m_2)}\right\}^{\frac{1}{2}}},$$

where $\frac{e}{A}$ may be put equal to a constant K.

We will suppose that the motion of an ion through a gas is regulated by the forces of attraction between the ion and the neutral molecules. An expression for B may then be obtained from the following considerations. The attraction of a charge e by a spherical conductor of electricity is given by $\frac{e^2 a^3 (2f^2 - a^2)}{f^3 (f^2 - a^2)^2}$, where f is the distance of the charge from the centre of the conductor whose radius is a. The writer has brought forward some evidence that the atom is spherical in shape, and if we assume that it is a perfect conductor of electricity, this expression gives the attraction between a charge e and an atom. When f is large in comparison with a the expression becomes $\frac{2e^2 a^3}{f^5}$, the attraction varying then inversely as the fifth power of the distance of separation of atom and charge, and Maxwell's equation is therefore applicable. When considering the attraction between an ion and a neutral molecule we may neglect the chemical attraction, and the attraction is then given by $\frac{2e^2 a^3}{f^5}$. The volume of an atom, which is proportional to a^3, is according to Traube* proportional to $\sqrt{m}$, where m is the atomic weight, and B is therefore proportional to $\sqrt{m}$, or in the case of a molecule proportional to $\Sigma\sqrt{m}$. The equation for the velocity now becomes

$$V = K_2 \frac{TR}{m_2 p_2} \left\{\frac{m_2 (m_1 + m_2)}{m_1 . \Sigma\sqrt{m}}\right\}^{\frac{1}{2}},$$

where K_2 is a constant.

* *Phys. Zeit.* October 1909, p. 667.

If the ion and the neutral molecule in a gas are of the same mass the velocity becomes $\frac{K_2RT}{p_2 m_2^{\frac{1}{2}}} \frac{1{\cdot}45}{(\Sigma\sqrt{m})^{\frac{1}{2}}}$. If the mass of the ion is large in comparison with that of the neutral molecule the velocity becomes $\frac{K_2RT}{p_2 m_2^{\frac{1}{2}}} \frac{1}{(\Sigma\sqrt{m})^{\frac{1}{2}}}$. Thus the velocity of the stable ion depends very little on its mass when it is greater than that of a molecule of the gas through which it moves. We have seen that the change in the clustering of the ion has the effect of making the average velocity of two different ions lie nearer to one another in magnitude than those of the simple ions. The average velocity of two ions, the masses of whose nuclei ions are not smaller than that of a neutral molecule, might therefore in practice be the same.

This result is interesting in connection with some experiments of A. Blanc* and Wellish† on the velocity of ions in different gases. Both these experimenters found that the positive ion made from a molecule passes through a gas of molecules of smaller mass with the same velocity as an ion made from one of the molecules of the gas. Wellish explains these results by supposing that a transfer of the electric charge from one molecule to another takes place during a collision, so that on the average we are dealing with the same kind of nuclei. It appears, however, that this result could also be produced in the way explained. On the whole it follows that the results on the velocity of ions cannot be interpreted with certainty since we are dealing with a statistical effect.

When the free ion is smaller than the neutral molecule of the gas, as is the case with the negative ion, the velocity is given by $V = \frac{K_2RT}{p_2 m_1^{\frac{1}{2}}} \frac{1}{(\Sigma\sqrt{m})^{\frac{1}{2}}}$, where m_1 is the mass of the ion. The velocity of the ion varies much more with its mass in this case than when its mass is larger than that of a molecule of the surrounding gas. But the average velocity of an ion cluster probably does not depend much on the mass of the free ion or simple cluster, as is the case when the free ions have a greater mass than that of a neutral molecule. For the change in potential energy when a cluster is formed is probably greater in the former case than in the latter, and the life of a free ion thus increases with its mass, or the greater the velocity of an ion the shorter is its life. On the whole the average velocity of two different ions whose nuclei are smaller in mass than that of a molecule of the gas through which they pass may therefore not differ more from

* *C. R.* CXLVII. July 1908, pp. 39—42.
† *Roy. Soc. Proc.* Ser. A, LXXXII. July 31, 1909, pp. 500—517.

one another than the velocities of two ions whose nuclei have a greater mass than that of a molecule of the gas. However, a difference in velocity, if it exists, would be more apparent in the former case than in the latter. No experiments seem to have yet been carried out to see whether the velocity of an ion depends on the mass of its nuclei when this has a much smaller mass than that of a molecule of the surrounding gas.

The equation for the velocity of a stable ion shows that if the temperature is kept constant the velocity varies inversely as the pressure, a result we assumed in a previous part of the paper.

The equation may also be written $V = \frac{K}{\rho_2}\left\{\frac{m_2(m_1+m_2)}{m_1 B}\right\}^{\frac{1}{2}}$. We see then that if the density of the gas is kept constant the velocity is independent of the temperature. The variation of the average velocity of an ion with temperature observed by Philips, who found that the velocity is approximately proportional to the temperature, must be due to the variation of the quantities $H_1, H_2 \ldots$, with the temperature, which appear in the equation for the average velocity of an ion.

The Heat of Combustion of a Molecule and its Chemical Attraction Constant. By R. D. KLEEMAN, B.A., Emmanuel College, D.Sc. (Adelaide), Mackinnon Student of the Royal Society; and Clerk Maxwell Student of the University of Cambridge. (Communicated by Mr A. Wood.)

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In previous papers the writer has deduced from surface tension and latent heat data the law of attraction between molecules that corresponds to the attraction which is large in comparison with gravitation for small distances of separation of the molecules. According to this law the attraction between two atoms is proportional to the product of the square roots of their atomic weights. The square root of the atomic weight of an atom was called its attraction constant. The attraction constant of a molecule is approximately equal to the sum of the attraction constants of its atoms. It is very probable that the law obtained holds for closer distances of separation of two atoms or molecules than the distance of separation of the molecules in a liquid. The attraction represented by the law would then be the only one operating when chemical combination takes place. If that is the case we would expect that relations exist between the chemical quantities connected with substances and the attraction constants of the atoms of their molecules. Such relations exist; we have already pointed out a number in a previous paper*. Further relations will be given in this paper. It should be mentioned that these relations can only as yet be found by trial; the relations given in this paper, relating to the heat of combustion of a molecule, have thus been obtained.

It was found that the heats of combustion of the hydrocarbons are approximately proportional to $\Sigma\sqrt{m_{HC}}$, which denotes the sum of the square roots of the atomic weights of the atoms of a molecule, and is therefore its attraction constant. This is shown by Table I which contains the ratios of the heats of combustion H_c to the quantity $\Sigma\sqrt{m_{HC}}$. It will be seen that this ratio is approximately constant. Its mean value is equal to 29·5. The serious deviation from constancy in the case of 'Acetylen' may be due to a partial polymerization of its molecules, in which case $\Sigma\sqrt{m_{HC}}$ would have to be multiplied by a factor corresponding to the extent of the polymerization, which would reduce the ratio to its proper value.

The heats of combustion given in this paper are taken from Landolt and Börnstein's *Tables*, 3rd edition, and are expressed in

* *Phil. Mag.* December, 1910, pp. 905—921.

kilogram calories. The names of the substances are in German, as the considerable labour of looking up the exact English equivalents was thus avoided. It should cause no inconvenience as the substances will easily be recognised by their German names.

It is remarkable that the above property of the H and C atoms persists in all compounds of H and C atoms with other atoms, which is brought out by subtracting quantities from the heat of combustion expressing the effect of the additional kinds of atoms. Thus in all compounds of H, C, and O atoms that were examined it was found that

$$\frac{H_c + n\,50{\cdot}7}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where $\Sigma\sqrt{m_{HC}}$ denotes as before the sum of the square roots of the atomic weights of the H and C atoms in a molecule, and n the number of O atoms it contains. This is shown by Table II, which contains substances representing the mon- and multi-atomic alcohols, carbohydrates, phenols, aldehydes, ketones, basic and oxy-acids.

The effect of the O atom on the heat of combustion as far as this relation is concerned is thus equal to $-50{\cdot}7$, and $50{\cdot}7$ must therefore be added per atom to the heat of combustion to obtain the effect due to the H and C atoms.

Table III contains compounds whose molecules are made up of H, C, N, and O atoms. In the case of the amido-acids, acid amido compounds, and nitrile acids, and the uric acid group, we have

$$\frac{H_c + n50{\cdot}7 + m5}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where m denotes the number of nitrogen atoms in a molecule. This relation is borne out by the third and sixth column of the table. It will be seen that the effect of the O atom in a molecule is the same as in a molecule containing only H, C, and O atoms. The effect of a N atom is equal to -5, and is thus small in comparison with that of an O atom, viz. $-50{\cdot}7$.

The nitro derivatives in the table do not fall into line with the other compounds. In their case we have

$$\frac{H_c + r21{\cdot}1}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where r denotes the number of NO_2 groups in a molecule. If we assume that an O atom has the same effect in these compounds as in those considered previously, which is very likely, we obtain that the effect of a N atom is equal to 80·3. This is numerically much larger than when the N atom occurs in one of the compounds

just considered, and is of a different sign. The equation for the nitro derivatives may accordingly be written

$$\frac{H_c + n50{\cdot}7 - m80{\cdot}3}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately.}$$

In Table IV compounds are given whose molecules contain N atoms only besides H and C atoms. The relation

$$\frac{H_c - m7{\cdot}3}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately}$$

holds for the amines. It will be seen that the effect of a N atom in these compounds is different from that in the compounds considered previously, but on the whole it is small.

The relation

$$\frac{H_c - m29{\cdot}5}{\Sigma\sqrt{m_{HC}}} = 29.5$$

holds approximately for the cyanides in the table. There is thus a considerable difference between their behaviour and that of the amines.

Table V contains some chlorides, bromides, and iodides. The heats of combustion of the chlorides in the first part of the table are subject to the relation

$$\frac{H_c + c13{\cdot}6}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

and those in the second part to the relation

$$\frac{H_c + c6{\cdot}5}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where c denotes the number of Cl atoms in a molecule. The effect of a Cl atom in the latter case is thus about half that in the former.

In the case of the bromides we have

$$\frac{H_c + u5{\cdot}8}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where u denotes the number of Br atoms in a molecule.

For the iodides we have

$$\frac{H_c - w9{\cdot}4}{\Sigma\sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where w denotes the number of I atoms in a molecule.

The effects of the atoms Cl, Br, and I on the heat of combustion of compounds of the same type are respectively $-13{\cdot}6$, $-5{\cdot}8$, and $9{\cdot}4$, and thus increase algebraically with the increase of atomic weight of the atoms.

The thio-alcohols given in Table VI fall into two groups. For the first group in the table we have

$$\frac{H_c - s136}{\Sigma \sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately,}$$

where s denotes the number of sulphur atoms in a molecule. For the second group we have

$$\frac{H_c - s78{\cdot}7}{\Sigma \sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately.}$$

The effect of an atom of sulphur on the heat of combustion in the latter case is thus about half that in the former.

The first part of the second column of Table VII contains some carbon dioxide derivatives. The heat of combustion in this case is subject to the relation

$$\frac{H_c - s78{\cdot}7 + c6{\cdot}5}{\Sigma \sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately.}$$

It will be seen that the values of the effects of a Cl and S atom on the heat of combustion are the same as some of the values found previously.

The first part of the first column of the table contains some acids which contain Cl and I atoms in the molecule. It was found that

$$\frac{H_c + n50{\cdot}7 + c13{\cdot}6 - w9{\cdot}4}{\Sigma \sqrt{m_{HC}}} = 29{\cdot}5 \text{ approximately}$$

applies to them. The effect of a O, Cl, and I atom in the compounds is thus the same as that in some of the compounds we have already considered.

There are a few additional compounds of a complex nature which fall under the chemical groups considered in this paper, but which do not fit in with other compounds in the above way. They are so few in number and so diverse in character that the laws they obey cannot yet be formulated.

A comparatively large number of the urea derivatives do not fit in with the compounds already considered. Thus ten of the compounds given in Table VII fit in with the relation

$$\frac{H_c + n50{\cdot}7 + m5 - s136}{\Sigma \sqrt{m_{HC}}} = 29{\cdot}5,$$

but the rest do not. It does not seem possible to obtain another relation to fit the remaining compounds or some of them, but each seems a special case. The heterocyclic compounds given at the end of the table fit in, however, with the results already obtained.

The deviations of compounds in behaviour from the group to which they belong are of great interest, in connection with

tereo-chemical considerations. The grouping of the atoms of a nolecule in space must be intimately connected with the heat of ombustion, and therefore with the relation appertaining to it. When more data are available to admit of a further extension of he results obtained, they should lead to results of importance in his connection. It will be found of interest to compare the results n this paper with those obtained in a previous paper*.

The relations in this paper can be transformed into a form in hich the denominator of the fraction is the sum of the square ots of the atomic weights of the atoms in a molecule, or is the ttraction constant of the molecule. The value of the fraction is ot altered by adding to the numerator and denominator quanties proportional to each of them respectively, and the relation n the above form is therefore obtained by adding $29{\cdot}5\Sigma\sqrt{m_n}$ o the numerator and $\Sigma\sqrt{m_n}$ to the denominator, where $\Sigma\sqrt{m_n}$ enotes the sum of the square roots of the atomic weights of the toms in a molecule besides the H and C atoms. For example, he relation

$$\frac{H_c + n\,50{\cdot}7}{\Sigma\sqrt{m_{\mathrm{HC}}}} = 29{\cdot}5,$$

hich applies to compounds containing H, C, and O atoms, may e written

$$\frac{H_c + n\,50{\cdot}7 + 29{\cdot}5n\sqrt{4}}{\Sigma\sqrt{m_{\mathrm{HCO}}}} = \frac{H_c + n\,109{\cdot}7}{\Sigma\sqrt{m_{\mathrm{HCO}}}} = 29{\cdot}5,$$

here $\Sigma\sqrt{m_{\mathrm{HCO}}}$ is the attraction constant of a molecule.

We can also deduce by the help of these relations formulae r the heat of formation of compounds. Take for example the ydro-carbons. Suppose that x grm. molecules of O_2 enter into ombustion with a grm. molecule of a hydro-carbon, causing the rmation of y grm. molecules of water and z grm. molecules of O_2. The numerical values of x, y, and z can of course at once e obtained from a consideration of the chemical formula of the ydro-carbon. And let A, B, and C denote the heats of formation f a grm. molecule of O_2, H_2O, and CO_2, respectively. The heat f formation H_F of a grm. molecule of the hydro-carbon is then btained from the equation

$$H_F + xA - yB - zC = H_c,$$

nd therefore

$$H_F = 29{\cdot}5\Sigma\sqrt{m_{\mathrm{HC}}} - xA + yB + zC.$$

f A, B, and C are known the value of H_F can thus at once be alculated for each hydro-carbon.

* *Loc. cit.*

TABLE I.

Name of substances (in German, taken from Landolt and Börnstein's Tables)	H_c	$\frac{H_c}{\Sigma \sqrt{m_{HC}}}$	Name of substances (in German, taken from Landolt and Börnstein's Tables)	H_c	$\frac{H_c}{\Sigma \sqrt{m_{HC}}}$
Methan ... ... CH_4	213·5	28·63	Toluol ... ... C_7H_8	933·8	28·92
Ethan ... ... C_2H_6	372·3	28·80	*o*-Zylol ... ... C_8H_{10}	1084·2	28·77
Athylen ... ... C_2H_4	341·1	31·24	Styrol ... ... C_8H_8	1045·5	29·22
Acetylen ... ... C_2H_2	313·8	35·18	Menthen ... ... $C_{10}H_{18}$	1523·1	28·95
Propan ... ... C_3H_8	528·4	28·74	Camphen ... ... $C_{10}H_{16}$	1469·2	29·34
Propylen ... ... C_3H_6	499·3	30·49	Naphtalin ... ... $C_{10}H_8$	1241·8	29·13
Allylen ... ... C_3H_4	473·0	32·91	Diphenyl ... ... $C_{12}H_{10}$	1510·1	29·31
Butan ... ... C_4H_{10}	687·2	29·19	Diphenylmethan ... ... $C_{13}H_{12}$	1659·9	29·12
Isobutylen ... ... C_4H_8	650·2	29·77	Di benzyl ... ... $C_{14}H_{14}$	1830·2	29·31
Amylen ... ... C_5H_{10}	804·0	29·45	Stilben ... ... $C_{14}H_{12}$	1777·3	29·41
Hexan ... ... C_6H_{14}	991·2	28·52	Tolan ... ... $C_{14}H_{10}$	1738·2	29·74
Hexahydrobenzol ... ... C_6H_{12}	933·2	28·49	Reten ... ... $C_{18}H_{18}$	2325·2	28·96
Tetrahydrobenzol ... ... C_6H_{10}	892·0	29·00	Chrysen ... ... $C_{18}H_{12}$	2140·3	28·80
Di hydrobenzol ... ... C_6H_8	848·0	29·48	Tryphenylmethan ... ... $C_{19}H_{16}$	2387·3	29·20
Benzol ... ... C_6H_6	784·1	30·68	Triphenylbenzol ... ... $C_{24}H_{18}$	2938·3	29·02
Heptan ... ... C_7H_{16}	1152·3	28·65	Tetraphenylmethan ... $C_{25}H_{20}$	3104·1	29·15

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Monatomic alcohols			
Methyl alcohol	CH_4O	170·6	29·65
Methyl äther	C_2H_6O	344·2	30·56
Ethyl alcohol	C_2H_6O	325·7	29·12
Ethyl äther	$C_4H_{10}O$	651·7	29·45
n-propyl alcohol	C_3H_8O	480·3	28·88
Allyl alcohol	C_3H_6O	442·7	30·01
Isobutyl alcohol	$C_4H_{10}O$	636·7	28·85
Trimethyl karbinol	$C_4H_{10}O$	632·8	28·67
Gärungs amyl alcohol	$C_5H_{12}O$	793·9	28·81
Furfur alcohol	$C_5H_6O_2$	612·8	29·38
Benzyl alcohol	C_7H_8O	895·2	29·35
Menthol	$C_{10}H_{20}O$	1509·2	28·57
Borneol (rac)	$C_{10}H_{18}O$	1476·5	29·03
Diphenyl karbinol	$C_{13}H_{12}O$	1613·9	29·20
Triphenyl karbinol	$C_{19}H_{16}O$	2342·0	29·26
Multiatomic alcohols			
Glykol	$C_2H_6O_2$	283·3	29·78
Saliginin	$C_7H_8O_2$	846·0	29·44
Glycerin	$C_3H_8O_3$	397·1	29·88
Eurythrit	$C_4H_{10}O_4$	502·6	29·59
Arabit	$C_5H_{12}O_5$	612·0	30·49
Mannit	$C_6H_{14}O_6$	728·5	29·71

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Carbohydrates			
Arabinose	$C_5H_{10}O_5$	557·1	27·42
Glucose	$C_6H_{12}O_6$	677·2	29·95
Rohrzucker	$C_{12}H_{22}O_{11}$	1355·0	29·88
Dextrin	$C_6H_{10}O_5$	667·2	29·62
Phenols			
Phenol	C_6H_6O	736·0	29·40
Anisol	C_7H_8O	905·5	29·57
Phenetol	$C_8H_{10}O$	1057·2	29·41
Brenzkatechin	$C_6H_6O_2$	685·2	28·28
Pyrogallol	$C_6H_6O_3$	633·3	29·35
o-Kresol	C_7H_8O	879·8	28·81
Anethol	$C_{10}H_{12}O$	1324·2	29·50
Eugenol	$C_{10}H_{12}O_2$	1286·9	29·77
Thymol	$C_{10}H_{14}O$	1350·0	28·82
a-Naphtol	$C_{10}H_8O$	1188·5	31·42
Aldehydes			
Methylal	$C_3H_8O_2$	462·5	30·68
Acetaldehyd	C_2H_4O	279·1	30·27
Metaldehyd	$(C_2H_4O)_3$	805·8	29·24
Acetal	$C_6H_{14}O_2$	923·2	29·48
Propylaldehyd	C_3H_6O	434·3	29·59

TABLE II (*continued*).

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Aldehydes (continued)			
Crotonaldehyd	C_4H_6O	542·3	29·89
Benzaldehyd	C_7H_6O	841·7	29·44
Salicylalaldehyd ...	$C_7H_6O_2$	807·6	29·99
Anisaldehyd	$C_8H_8O_2$	967·3	29·96
Zimtaldehyd	C_9H_8O	1112·9	29·72
Vanillin	$C_8H_8O_3$	914·7	28·21
Glyoxal	$C_2H_2O_2$	172·4	30·68
Aldol	$C_4H_8O_2$	546·9	29·68
Furfurol	$C_5H_4O_2$	559·8	31·03
Ketones			
Aceton	C_3H_6O	426·9	29·10
Acetylaceton	$C_5H_8O_2$	616·3	28·37
Actophenon	C_8H_8O	988·5	29·11
Bezophenon	$C_{13}H_{10}O$	1558·1	29·27
Benzolaceton	$C_{10}H_{10}O$	1258·1	29·36
Di benzolaceton	$C_{17}H_{14}O$	2089·0	29·38
Benzoin	$C_{14}H_{12}O_2$	1672·5	29·34
d-Kampher	$C_{10}H_{16}O$	1414·3	28·75
Chinon	$C_6H_4O_2$	656·8	30·62
Anthrachinon	$C_{14}H_8O_2$	1548·5	29·21

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Monobasic acids			
Ameisensäure	CH_2O_2	61·7	29·87
Ameisensäuremethylester	$C_2H_4O_2$	233·2	30·64
Ameisensäureäthylester	$C_3H_6O_2$	388·0	29·88
Essigsäure	$C_2H_4O_2$	209·4	28·46
Essigsäureanhydrid ...	$C_4H_6O_3$	431·9	29·43
Essigsäuremethylester ...	$C_3H_6O_2$	395·3	30·33
Essigsäureäthylester ...	$C_4H_8O_2$	537·1	29·86
Propionsäure	$C_3H_6O_2$	367·4	28·62
n-Valeriansäure	$C_5H_{10}O_2$	681·8	28·68
n-Buttersäure	$C_4H_8O_2$	524·4	28·65
Crotonsäure	$C_4H_6O_2$	478·0	29·20
Angelikasäure	$C_5H_8O_2$	635·1	29·13
n-Capronsäure	$C_6H_{12}O_2$	830·2	29·33
Sorbinsäure	$C_6H_8O_2$	728·9	28·49
Benzöesäure	$C_7H_6O_2$	772·8	28·92
Benzöesäuremethylester	$C_8H_8O_2$	944·0	29·22
Benzöesäureäthylester ...	$C_9H_{10}O_2$	1099·3	29·18
Benzöesäurephenylester	$C_{13}H_{10}O_2$	1505·2	29·21
Phenylessigsäure ...	$C_8H_8O_2$	933·2	29·00
Zimtsäure	$C_9H_8O_2$	1042·3	29·22
Caprinsäure	$C_{10}H_{20}O_2$	1458·3	28·56

TABLE II (*continued*).

Name of substances (in German, taken from Landolt and Börnstein's Tables)	H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Monobasic acids (*continued*)		
Palmitinsäure ... ... $C_{16}H_{32}O_2$	2371·8	28·31
Stearinsäure ... ... $C_{18}H_{36}O_2$	2711·8	28·62
Ölsäure ... ... $C_{18}H_{34}O_2$	2682·0	28·89
Di and multibasic acids		
Oxalsäure ... ... $C_2H_2O_4$	60·2	29·58
Oxalsäuredimethylester ... $C_4H_6O_4$	402·1	30·68
Oxalsäurediäthylester ... $C_6H_{10}O_4$	716·2	29·88
Malonsäure ... ... $C_3H_4O_4$	207·3	28·52
Malonsäuredimethylester $C_5H_8O_4$	552·5	29·86
Malonsäurediäthylester ... $C_7H_{12}O_4$	860·6	29·45
Bernsteinsäure ... ... $C_4H_6O_4$	356·8	28·76
Bernsteinsäuredimethylester $C_6H_{10}O_3$	708·5	29·63
Bernsteinsäurediäthylester $C_8H_{14}O_4$	1007·7	29·05
Fumarsäure ... ... $C_4H_4O_4$	320·1	29·95
Maleinsäureanhydrid ... $C_4H_2O_3$	336·4	30·83
Acetylendikarbonsäure ... $C_4H_2O_4$	306·2	32·13
Glutarsäure ... ... $C_5H_8O_4$	515·0	28·37
Itaconsäure ... ... $C_5H_6O_4$	477·5	29·20
Adipinsäure ... ... $C_6H_{10}O_4$	668·9	28·34
Pimilinsäure ... ... $C_7H_{12}O_4$	828·9	28·48

Name of substances (in German, taken from Landolt and Börnstein's Tables)	H_c	$\frac{H_c+n50{\cdot}7}{\Sigma\sqrt{m_{HC}}}$
Di and multibasic acids (*continued*)		
Hexahydroterephtasäure ... $C_8H_{12}O_4$	928·6	29·68
o-Phtalsäure ... ... $C_8H_6O_4$	771·6	28·94
Phtalsäureanhydrid ... $C_8H_4O_3$	784·0	29·55
Isopthalsäure ... ... $C_8H_6O_4$	768·8	28·85
d-Kamphersäure ... ... $C_{10}H_{16}O_4$	1241·8	28·55
Trikarballylsäure ... ... $C_6H_8O_6$	515·0	28·48
Mellithsäure ... ... $C_{12}H_6O_{12}$	788·2	29·38
Oxy acids		
Glykolsäure ... ... $C_2H_4O_3$	186·0	30·88
Glycolid ... ... $C_2H_2O_2$	167·4	30·13
Zitronensäure ... ... $C_6H_8O_7$	474·6	28·84
Salicylsäure ... ... $C_7H_6O_3$	727·1	29·09
Milchsäure ... ... $C_3A_6O_3$	329·5	29·40
Milchsäureäthylester ... $C_5H_{10}O_{13}$	656·0	29·60
Tartronsäure ... ... $C_3H_4O_5$	165·8	29·16
d-a-l-Weinsäure ... ... $C_4H_6O_6$	281·0	29·50
Lavulinsäure ... ... $C_5H_8O_3$	577·4	28·83
Salicylsäuremethylester .. $C_8H_8O_3$	898·1	29·48
Salicylsäureäthylester ... $C_9H_{10}O_3$	1051·7	29·28
Gallussäure ... ... $C_7H_6O_5$	634·1	29·37
Acetessigsäure ... ... $C_6H_{10}O_3$	753·6	30·05

TABLE III.

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7+m5}{\Sigma\sqrt{m_{HC}}}$
Amido acids			
Glykokol	$C_2H_5NO_2$	234·9	29·30
Hippursäure ...	$C_9H_9NO_3$	1012·9	29·16
Sarkosin	$C_3H_7NO_2$	401·2	29·22
Kreatin	$C_4H_9N_3O_2$	560·0	29·61
Alanin	$C_3H_7NO_2$	389·2	28·52
Amidobernsteinsäure	$C_4H_7NO_4$	386·8	28·54
Asparagin	$C_4H_8N_2O_3$	448·1	27·94
Leucin	$C_6H_{13}NO_2$	855·9	28·50
Tyrosin	$C_9H_{11}NO_3$	1071·2	29·14
Acid amido compounds			
Foramid	CH_3ON	134·9	29·50
Acetamid	C_2H_5ON	288·1	28·84
Propionsäureamid ...	C_3H_7ON	436·0	28·26
Benzamid	C_7H_7ON	852·3	29·08
Oxamid	$C_2H_4O_2N_2$	203·3	28·82
Oxaminsäure ...	$C_2H_3O_3N$	128·8	28·82
Malonamid	$C_3H_6O_2N_2$	358·8	28·71
Succinamid	$C_4H_8O_2N_2$	509·7	28·44
Succinimid	$C_4H_5O_2N$	438·1	29·27
Phtalimid	$C_8H_5O_2N$	850·2	29·50

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c+n50{\cdot}7+m5}{\Sigma\sqrt{m_{HC}}}$
Nitrile acids			
Cyanessigsäure ...	$C_3H_3NO_2$	299·0	30·31
Cyanessigsäure methylester ...	$C_4H_5NO_2$	471·9	30·69
Cyanessigsäure ethylester ...	$C_5H_7NO_2$	629·7	30·29
Uric acid group			
Harnsäure	$C_5H_4N_4O_3$	461·4	29·74
Guanin	$C_5H_5N_5O$	586·6	29·70
Theobromin... ...	$C_7H_8N_4O_2$	846·0	30·02
Caffëin	$C_8H_{10}N_4O_2$	1016·0	30·18
Nitro derivatives			$\frac{H_c+r21{\cdot}1}{\Sigma\sqrt{m_{HC}}}$
Nitromethan ...	CH_2NO_2	169·8	29·5
Nitroäthan	$C_2H_5NO_2$	322·3	28·78
o-Dinitrobenzol ...	$C_6H_4(NO)_2$	703·5	30·11
symm. Trinitro benzol ...	$C_6H_3(NO)_3$	663·8	30·56

TABLE IV.

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c - m7{\cdot}3}{\Sigma\sqrt{m_{HC}}}$
Amines			
Methylamin	CH_5N	256·9	29·50
Di methylamin	C_2H_7N	426·0	30·08
Athylamin	C_2H_7N	409·7	28·87
Trimethylamin	C_3H_9N	592·0	28·91
Di äthylamin	$C_4H_{11}N$	724·4	29·08
Tri äthylamin	$C_6H_{15}N$	1047·0	28·92
Benzylamin	C_7H_9N	968·6	29·22
Anilin	C_6H_7N	818·5	29·16
Phenylhydrazin	$C_6H_8N_2$	805·8	27·51
Azobenzol	$C_{12}H_{10}N_2$	1555·8	29·90
Hydrazobenzol	$C_{12}H_{12}N_2$	1599·1	29·59
Methylanilin	C_7H_9N	974·0	29·10
Di methylanilin	$C_8H_{11}N$	1142·9	29·16
Di äthylanilin	$C_{10}H_{15}N$	1451·8	28·95
o-Toluidin	C_7H_9N	964·7	28·58
Di phenylamin	$C_{12}H_{11}N$	1536·9	28·97
p-Phenylendiamin	$C_6H_8N_2$	843·9	28·27
Tri phenylamin	$C_{18}H_{15}N$	2269·0	29·15
Benzidin	$C_{12}H_{12}N_2$	1560·9	29·74
Cyanides			$\frac{H_c - m29{\cdot}5}{\Sigma\sqrt{m_{HC}}}$
Blausäure	CHN	159·3	29·05
Acetonitril	C_2H_3N	291·6	26·40
Propionitril	C_3H_5N	446·7	27·10
Benzonitril	C_7H_5N	865·9	28·62
Toluylsäurenitril	C_8H_7N	1030·7	28·78
Cyan	C_2N_2	262·5	29·32
Malonitril	$C_3H_2N_2$	395·1	29·52
Bernsteinsäurenitril	$C_4H_4N_2$	545·0	27·20

TABLE V.

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c + c\,13{\cdot}6}{\Sigma\sqrt{m_{HC}}}$
Chlorides			
Methylchlorid	CH_3Cl	176·9	29·5
Chloroform	$CHCl_3$	107·0	30·09
Chloräthyl...	C_2H_5Cl	334·1	29·16
Athylenchlorid	$C_2H_4Cl_2$	296·4	29·63
Monochloräthylenchlorid ...	$C_2H_3Cl_3$	262·5	30·57
Monochloräthylen	C_2H_3Cl	298·3	29·60
Propylchlorid	C_3H_7Cl	492·4	29·12
Chloraceton	$C_3H_6Cl_2$	453·9	29·37
Monochlorpropylen	C_3H_5Cl	453·4	30·37
Isobutylchlorid	C_4H_9Cl	650·1	29·06
Phynylchlorid	C_6H_5Cl	763·9	30·18
			$\frac{H_c + c\,6{\cdot}5}{\Sigma\sqrt{m_{HC}}}$
Tetrakohlenstoff	CCl_4	75·9	29·5
Perchloräthylen	C_2Cl_4	195·1	31·94
			$\frac{H_c + u\,5{\cdot}8}{\Sigma\sqrt{m_{HC}}}$
Bromides			
Methylbromid	CH_3Br	184·7	29·5
Athylbromid	C_2H_5Br	341·8	29·16
Propylbromid	C_3H_7Br	499·3	29·07
Allylbromid	C_3H_5Br	462·1	30·42
			$\frac{H_c - w\,9{\cdot}4}{\Sigma\sqrt{m_{HC}}}$
Iodides			
Methyleniodid	CH_2I_2	178·4	29·23
Iodoform	CHI_3	161·9	29·98
Athyleniodid	$C_2H_4I_2$	324·9	28·03
Propyliodid	C_3H_7I	514·3	29·05
Allyliodid	C_3H_5I	478·3	30·49
Jodbenzol	C_6H_5I	770·7	29·56

TABLE VI.

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c - s136}{\Sigma \sqrt{m_{HC}}}$
Thio alcohols			
Ethylsulfhydrat	C_2H_6S	517·2	29·5
Ethylsulfid	$C_4H_{10}S$	829·6	29·09
Allylsulfid	$C_6H_{10}S$	1068·1	30·30
Amylsulfhydrat	$C_5H_{12}S$	992·0	29·21
Amylsulfid	$C_{10}H_{12}S$	1775·7	28·96
			$\frac{H_c - s78·7}{\Sigma \sqrt{m_{HC}}}$
Methylsulfid	CH_4S	298·8	29·5
Di methylsulfid	C_2H_6S	457·3	29·3
Di äthylsulfid	$C_4H_{10}S$	772·2	29·16

TABLE VII.

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c + n50·7 + c13·6 - w9·4}{\Sigma \sqrt{m_{HC}}}$
Acids			
Chloressigsäure ...	$C_2H_3ClO_2$	171·0	28·83
Trichloressigsäure ...	$C_2HCl_3O_2$	92·8	29·68
o-Jodbenzöesäure ...	$C_7H_5IO_2$	769·6	29·46
			$\frac{H_c + n50·7 + c6·5 - s78·7}{\Sigma \sqrt{m_{HC}}}$
CO_2 *derivatives*			
Phosgen	$COCl_2$	41·8	30·49
Kohlenstofoxysulfid	COS	131·0	29·27
Schwefelkohlenstoff	CS_2	265·1	31·13

TABLE VII (*continued*).

Name of substances (in German, taken from Landolt and Börnstein's Tables)		H_c	$\frac{H_c + n50{\cdot}7 + m5 - s136}{\Sigma\sqrt{m_{HC}}}$
Urea derivatives			
Harnstoff	CH_4ON_2	152·2	28·54
Thioharnstoff ...	CH_4N_2S	342·8	29·07
Guanidin	CH_5N_3	247·6	29·85
Monophenylharnstoff	$C_7H_8ON_2$	880·0	29·12
Diphenylharnstoff ...	$C_{13}H_{12}ON_2$	1612·8	29·36
Hydantoin	$C_3H_4N_2O_3$	311·9	28·75
Barbitursäure ...	$C_4H_4N_2O_3$	353·4	28·86
Uramill	$C_4H_5N_3O_3$	379·0	28·98
Alloxan	$C_4H_4N_2O_4$	276·5	27·39
Murexid	$C_8H_8N_6O_6$	736·7	30·02
Guanidin nitral	$CH_5N_3 . NO_3H$	207·8	39·63
Nitro guanidin ...	$CH_4N_4O_2$	210·3	44·46
Carbaminsäuresammon	$CO_2N_2H_6$	49·0	16·95
Allantoin	$C_4H_6N_4O_3$	413·8	35·46
Allxantin ...	$C_8H_6N_4O_8 . H_2O$	584·7	37·44
			$\frac{H_c + n50{\cdot}7 + m5}{\Sigma\sqrt{m_{HC}}}$
Heterocyclic compounds			
Pyridin	C_5H_5N	673·7	29·82
Pipiridin	$C_5H_{11}N$	834·7	28·23
Coniin	$C_8H_{17}N$	1275·5	28·39
Chinchinin ...	$C_{19}H_{22}N_2O$	2546·2	29·43
Chinin ...	$C_{20}H_{24}H_2O_2$	2663·7	29·05
			$\frac{H_c + m5 \quad w9{\cdot}4}{\Sigma\sqrt{m_{HC}}}$
Chinolin	C_9H_7N	112·3	29·25
Pyrrol	C_4H_5N	568·1	29·77
Jodol	C_4HI_4N	503·1	30·87
Indol	C_8H_7N	1022·5	30·35
			$\frac{H_c + r21{\cdot}1}{\Sigma\sqrt{m_{HC}}}$
Dioxindol	$C_8H_7NO_2$	915·7	28·67
Isatin	$C_8H_5NO_2$	867·8	28·97

On the Origin of Spectra. By Frank Horton, M.A., St John's College.

[*Read* 22 May 1911.]

In a paper recently communicated to the Royal Society*, the author has given an account of some experiments with mercury vacuum tubes which show that mercury is capable of giving several distinct line spectra when rendered luminous by an electrical discharge. The particular spectrum appearing in any given case depends upon the energy of the discharge in relation to the mass of vapour through which it passes. The spectrum most easily produced consists of five bright lines, but as the energy of the discharge is increased other spectra, recorded in the paper, make their appearance in turn. Reasons can be given for thinking that these more complicated spectra are due to the formation of definite electronic systems, which are practically unstable new substances formed from the normal mercury atoms by the passage of the discharge, and that they are not due merely to different modes of vibration of the electrons in some one system such, for instance, as the mercury atom.

In many respects mercury appears to be an ideal substance to use for investigating the origin of spectra. Its vapour is monatomic and can be rendered luminous in several ways: by the electric arc, or spark, or by the vacuum tube discharge. This latter may be produced (*a*) by an induction coil discharge with variable capacity and self-induction in the circuit, (*b*) by means of the low potential discharge from a glowing lime cathode, (*c*) by electro-magnetic induction in the electrodeless ring discharge. Under these different conditions a continuous spectrum, a band spectrum, and spectra with different numbers of bright lines may be obtained.

As the result of a careful investigation of the spectrum of mercury, Stark† has concluded that mercury possesses two distinct line spectra, that given by the arc *in vacuo* and that given by a vacuum tube discharge. These he identifies as being due to monovalent and to divalent atoms—atoms which have lost one and two electrons respectively. Stark's views on the origin of spectra may briefly be summarised as follows:

(1) Continuous spectra are due to freely moving electrons, the accelerations of which are continually being changed.

* *Roy. Soc. Proc.* 1911.

† Stark, *Ann. d. Phys.* xvi. 1905, p. 490.

(2) Line spectra are due to the vibrations of the electrons contained in the positive ions, all the lines of a series being due to the same source; but a single positive ion may be the source of several series of lines at the same time.

(3) Band spectra are due to electrically neutral bodies, and are formed in the act of combination of the negative electron with the positive ion.

In addition to the conclusion that mercury should have two distinct line spectra, Stark also holds that there should be two distinct band spectra, one formed by the combination of a divalent positive ion with a negative electron to form a monovalent ion, the other produced when the monovalent ion unites with another electron to form a neutral atom.

These views of Stark have been criticised by W. Wien*, who, from observations of the effect of a magnetic field on canal rays formed in various vapours and gases, has come to the conclusion that the carriers responsible for the line spectra are neutral atoms, and that the vibrations producing the luminosity are caused by the recombination of negative electrons with the positive "remainder atoms." This is the view which is, I think, supported by the result of my recent observations of the spectra of mercury under different electrical conditions. In the paper already referred to five distinct line spectra are recorded. These, I think, are due to the recombinations of remainder atoms of different "electric atomic weights" with the appropriate number of negative electrons to form neutral systems. These systems are probably not similar in all respects to the atoms of the unionised gas, but are less stable arrangements of positive ions with one or more negative electrons revolving round them—each system being electrically neutral. The periods of these systems would depend upon the arrangement of the electrons around the central positive ion. There would be different equilibrium positions and consequently several possible periods from any one system. These would be affected by a magnetic field in such a way as to account for the Zeeman effect.

The fact that compounds always give banded spectra would seem to indicate that these are due, not to electrons, but to the vibrations of larger bodies. Since they produce light of the same wave length, these larger bodies must be under the influence of more intense forces, which suggests that they are not separate atoms, but systems of atomic dimensions vibrating inside the molecule itself. On these views of the origin of line and of band spectra we should expect that a gas or vapour consisting solely of molecules in a normal condition would give a band spectrum, a

* Wien, *Ann. d. Phys.* xxx. 1909, p. 349.

onclusion which is borne out by the fact that the absorption pectra of such gases always consist of bands. In the case of the apours of the alkali metals, which give line spectra, we have nolecules which are not in a "normal" condition, as is shown by he abnormal conductivity of these vapours.

To obtain the emission spectrum of a gas we have to render it uminous by an electric discharge, and the effect of this is to ionise he molecules and to alter the composition of the gas. Electrons re set free, positive ions are produced, and, by the collisions f these, vibrating systems are formed which radiate the energy of he spectrum lines. This difference in the composition of the gas s clearly shown by the experiments of Ladenburg* and of Pflüger† n the absorption of light by hydrogen. These experimenters could et no absorption of light by the gas in the normal condition, but ound distinct absorption of the red and other lines when light was assed through a long tube containing the gas at a pressure of a ew centimetres, conveying an electric current. Evidently these ines are due to something which does not exist in the gas in the ormal state, but is produced in it by the passage of the discharge. Similar results have been obtained with mercury vapour. The bsorption of this was first investigated by Lockyer‡, and later by Strutt§; neither observer was able to obtain any absorption in he luminous spectrum, but more recently Wood‖ has shown that here is absorption in the ultra-violet. That ionised mercury vapour does produce absorption has been demonstrated by Küch nd Retschinsky¶, and also by Pfluger**. The method consists n having two mercury arc lamps placed one behind the other, and n measuring the percentage absorption of the light from the first amp in passing through the second, in the case of certain definite ines of the visible spectrum. The results showed that ionised mercury vapour possesses the power of absorbing those rays which t emits, whereas the vapour in the normal condition produces no bsorption.

We thus see that ionised gases and vapours contain electronic ystems which are not present in them in the normal state. These ystems are the "molecules" of new substances formed from the riginal gas or vapour by the passage of the electric discharge. call them "new substances" because it is probable that they ossess chemical properties different from those of the original

* Ladenburg, *Deutsch. Phys. Gesell.* Verh. x. 14, 1908, p. 550.
† Pflüger, *Ann. d. Phys.* xxiv. 3, 1907, p. 515.
‡ Lockyer, *Roy. Soc. Proc.* xxii. 1874, p. 374.
§ Strutt, *Phil. Mag.* vi. 1903, p. 76.
‖ Wood, *Astrophys. Jour.* xxvi. 1907, p. 41.
¶ Küch and Retschinsky, *Ann. d. Phys.* xxii. 1907, p. 852.
** Pflüger, *Ann. d. Phys.* xxiv. 3, 1907, p. 515.

substance. A simple experiment due to Dr H. Brereton Baker* shows that ionised mercury vapour has at least one different chemical property from mercury vapour in the ordinary atomic condition; for if oxygen is allowed to enter a mercury lamp immediately after the current has been cut off, it is found that a considerable quantity of mercuric oxide is formed, although the temperature is much lower than that at which mercury vapour in a normal condition combines with oxygen.

The recent experiments of Sir J. J. Thomson† have shown that the carriers of positive electricity in a vacuum tube are often more complex than the original gas or vapour through which the discharge is passing. Thus in the case of oxygen gas, carriers of positive electricity with "electric atomic weights" 8, 16, 32, 48, and 96, have been discovered. The first of these corresponds to the atom of oxygen with two positive charges, O_{++}; the second to the atom with one positive charge, O_+; the third to the oxygen molecule $(O_2)_+$; the fourth to the molecule of ozone $(O_3)_+$; and the fifth to $(O_6)_+$. The vibrations of each of these positive ions may give rise to luminous radiation, or this may come from neutral systems formed by collisions with electrons. The vibrations of these neutral systems would, on Wien's theory, give rise to spectrum lines. On the other hand we should expect that if the vibrations of the carriers of greater "electric atomic weight" give rise to luminous radiation, its spectrum would consist of bands, and it is well known that bands, especially in the green, are the characteristic feature of the spectrum of oxygen at low pressures. At higher pressures the bands are not so marked, which is the result to be expected, for the more frequent collisions would tend to prevent the formation of complicated molecules.

In the case of mercury vapour Professor Thomson has detected positive carriers with electric atomic weights of 800, 200, 100, and 66, corresponding to $(Hg_4)_+$, Hg_+, Hg_{++}, and Hg_{+++}, respectively. As in the case of oxygen, it seems probable that it is the vibrations of large atomic aggregates such as (Hg_4) which are the origin of the band spectrum observed by Eder and Valenta‡, Huff§ and others. If Wien's view is correct it is the carriers of smaller mass which, by their collisions with free electrons, form the systems producing the various spectrum lines, and the different line spectra which the author has observed are probably due to the different neutral systems formed. More energy would be required for the formation of a positive ion with three charges than for the formation of an ion with two charges or with unit charge, and so

* Baker, *Nature*, LXXXIV. 1910, p. 388.
† Thomson, *Phil. Mag.* XXI. 1911, p. 225.
‡ Eder and Valenta, *Denkschrift. Wien. Akad.* LXI. 1894, p. 401.
§ Huff, *Astrophys. Jour.* XII. 1900, p. 103.

e neutral systems containing positive ions with the smallest ectric atomic weights would be the last to be formed as the nergy of the discharge is increased. Since these systems contain e largest number of oscillating electrons, they are capable of oducing the greatest number of spectrum lines; so that we ould expect the spectrum with most lines to be formed when e discharge contains the greatest amount of energy. This is in greement with the experimental results, for the "many lined pectrum" of mercury is obtained when a heavy discharge with pacity in the circuit is passed through the vapour at a low ressure.

Since a definite minimum amount of energy may be expected be required for the production of any one form of positive ion, follows that the corresponding neutral system, and the lines to nich it gives rise, will appear when the energy is increased up to at value, and it is this which makes it possible to obtain several istinct spectra with quite definite changes from one to the other the electrical conditions are gradually altered. The new ectrum is not at its best when first visible, but the new lines t brighter as further change in the conditions of the discharge creases the number of systems emitting them. If the conditions the discharge are such as to form several types of radiating ntres at the same time, the spectrum contains the lines due to of them. The "many lined spectrum" observed by the author ntained all the lines of the other spectra with the exception of e in the red and orange regions, which were sometimes seen, but ere not visible when the spectrum was at its best.

The positive ionisation produced by phosphates when heated:
By Frank Horton, M.A., St John's College.

[*Read* 22 May 1911.]

In a paper recently communicated to the Society*, the author described some observations of the rate of discharge of positive electricity from sodium phosphate when heated in different gases at various pressures. The results of these experiments led to the conclusion that the gas molecules themselves play an active part in carrying the current from the hot anode to the neighbouring cathode.

In a recent number of the *Philosophical Magazine*† the view has been put forward by Dr W. Wilson that the positive leak obtained when aluminium phosphate is heated upon platinum is due mainly to the platinum, and Dr Wilson states that he could detect no positive electrification from aluminium phosphate heated upon a Nernst filament. This result is difficult to reconcile with the original experiment of Sir J. J. Thomson‡ whereby the large positive leak from hot aluminium phosphate was first detected. In that experiment the phosphate was heated, not upon platinum but upon a thin sheet of mica covering a porcelain tube, and very large quantities of positive electricity were given off. Professor Thomson used many different salts in his experiments and found that, whereas all the phosphates gave a large positive electrification, metallic oxides as a class gave a large excess of negative electricity when heated in a similar manner. It would therefore appear that the property of discharging positive or negative electricity belongs to the substance itself and not to the material used to support it during ignition.

The author has been continuing his observations on the positive ionisation produced by phosphates when heated, using the apparatus described in his former paper with lithium phosphate substituted for sodium phosphate. Observations have been made of the positive leak from lithium phosphate in air, in oxygen, in carbon monoxide, and in hydrogen, at pressures between and 30 mm. of mercury, under a saturation voltage of 40 volts

* Horton, *Proc. Camb. Phil. Soc.*, Vol. xvi. 1911, p. 89.
† Wilson, *Phil. Mag.* vi. Vol. xxi. 1911, p. 634.
‡ Thomson, *Proc. Camb. Phil. Soc.*, Vol. xiv. 1906, p. 105.

the observations in each case being made with the phosphate at 800° C.—the standard temperature of comparison used in the experiments with sodium phosphate. It was found that the positive ionisation produced by lithium phosphate in air is of about the same magnitude as that from sodium phosphate under similar conditions. The effect of substituting other gases for air was also of a similar nature to that found with sodium phosphate. The leak in oxygen was about the same as that in air; carbon monoxide increased the leak considerably, and there was a still further increase on replacing this latter gas by hydrogen.

In each gas observations were made at different pressures, a series of observations being taken with both decreasing and increasing pressures. The gradual alteration of the pressure was greatly facilitated by having in connection with the apparatus a large vertical glass tube, which could be filled with mercury by raising a cistern of mercury attached by india-rubber tubing to its lower end. Starting with any gas at a high pressure and gradually reducing this, the positive leak was found to increase slowly at first, but afterwards more rapidly, until a pressure of maximum leak was attained, usually between 0·1 and 0·3 mm. of mercury, after which the leak fell off very rapidly as the pressure was still further reduced. With gradually increasing pressures the reverse order was obtained, but the maximum value of the leak was not reached until a pressure higher than that giving the maximum leak with decreasing pressures. The maximum value of the positive leak was about the same whether the observations were taken at increasing or at decreasing pressures. I think this hysteresis effect could have been eliminated, and the same current-pressure curve have been obtained at both increasing and decreasing pressures, if a longer time had been allowed before taking each reading so as to enable the hot phosphate to get into equilibrium with the new pressure of the surrounding gas, but to do this a series of observations would have occupied many successive hours.

In the experiments with sodium phosphate the pressure of maximum leak was higher than in these experiments with lithium phosphate. The observations with the sodium salt were always taken at gradually diminishing pressures, for then I had not fixed up the arrangement I use now for gradually increasing the pressure, but the few observations which were made after letting a little extra gas into the apparatus showed no sign of the hysteresis effect found during the present experiments. A more complete set of observations at increasing pressures is needed to test this thoroughly, but it seems as if sodium phosphate attains equilibrium with the surrounding gas more quickly than lithium phosphate does.

The experiments with lithium phosphate heated in hydrogen have not yet been made as completely as I would wish, owing to the fine wires of the thermo-couple used to indicate the temperature of the anode having bent together and short circuited inside the apparatus while the first series of observations with this gas was being made, but I have obtained evidence of a pressure of maximum leak with hydrogen, as with air, oxygen, and carbon monoxide.

As recorded in my previous paper, a pressure of maximum positive leak was not obtained with sodium phosphate heated in hydrogen, but the current decreased continuously as the pressure was reduced from 20 mm. of mercury to a high vacuum. I am now inclined to think that the curve given for hydrogen (page 97) represents the final stage of the curves obtained with the other gases, and that experiments made over a greater range of pressures will show that, in hydrogen too, there is a pressure at which the positive leak from heated sodium phosphate has a maximum value.

The Transmission of Cathode Rays through Matter. By R. WHIDDINGTON, B.A., St John's College. (Communicated by Professor Sir J. J. THOMSON.)

[*Received* 5 July 1911.]

It has been known for some time that cathode rays lose velocity on passing through matter—the change being greater for slow than for fast rays. This fact was established by Leithauser*, who however did not establish any definite law of transmission. A similar effect exists in the case of β-rays, but it is so very small that the first attempt to detect it was a failure†.

Quite recently W. Wilson‡ has investigated the velocity change of β-rays transmitted through matter with the object of discovering the law of velocity diminution. He found himself unable to distinguish with certainty between relations of the type

$$v_0^4 - v_x^4 = a \cdot x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

and

$$v_0^2 - v_x^2 = a \cdot x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2),$$

where v_0 = the velocity of rays incident on a metal sheet of thickness x,

v_x = the velocity of the rays transmitted through the sheet.

Wilson came to the conclusion that (2) fitted his results rather better than (1), but his measurements are not accurate enough over a sufficiently wide range to decide. The β-rays used in Wilson's experiments possessed initial velocity (v_0) ranging between 2·85 and 2·48 $\times 10^{10}$ cms. per sec.

The experiments of this paper are merely Wilson's experiments carried out with cathode rays instead of β-rays.

The apparatus used is shown in the diagram (Fig. 1).

B and C are exactly similar brass cylinders (whose axes are at right angles to the plane of the paper) wound on the outside with thick copper wire in solenoid fashion§. When currents pass round these solenoids very uniform magnetic fields are set up within them and parallel to their axes. These currents are measured in both cases by the same Ammeter F by use of the specially designed rocking-key K. The glass tube D is about 3 cms. in diameter, and contains a magnetically controlled trolley

* Leithauser, *Ann. d. Phys.* xv. p. 283.

† Schmidt, *Phys. Zeit.* VIII. 1907, p. 361.

‡ Wilson, *Proc. Roy. Soc.* LXXXIV. A, p. 150.

§ The writer has previously described a solenoid wound cylinder of this type in *Proc. Camb. Phil. Soc.* 1911.

carrying various absorbing sheets. M and N are narrow parallel slits, ·06 cms. wide and about 5 cms. apart. They serve to limit the rays diverging from the metal sheet just above M to a very narrow cone. A is a glass bulb fitted with a regulating cathode E.

The bulb A, the solenoids B and C, and the tube D are all waxed together in the way shown in the diagram, the whole system being evacuated to something less than 1/100 mm. of mercury by liquid air and charcoal.

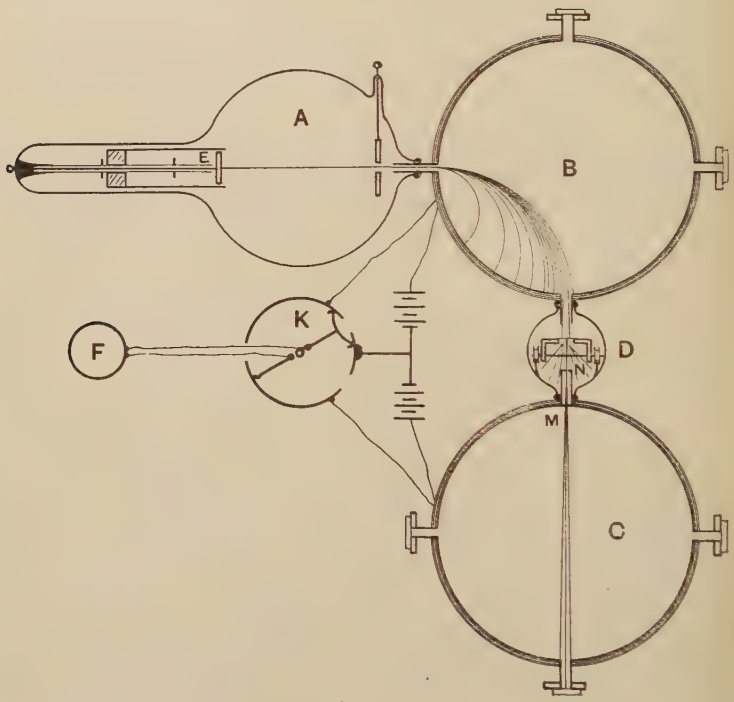


Fig. 1.

The parallel beam of cathode rays from E becomes split up into a "spectrum" on entering B, and only those rays which are bent through a right angle find themselves able to strike the absorbing sheet in D. The velocity of such rays is directly proportional to the current passing round the solenoid.

Some of the cathode rays striking this metal sheet are diffusely reflected, some are stopped altogether, but very many are transmitted with diminished velocity. These latter rays are allowed to traverse the cylinder C (in the figure there is supposed to be no current passing). The current required in the solenoid

C to deflect these rays through a right angle is a measure of their velocity. We thus have the means of measuring both v_0 and v_x.

As has been pointed out in a previous paper, a solenoid so short as the one here used while largely concentrating the field within itself sets up a small but appreciable external field. Such a field can be easily balanced out by means of a suitably placed coil in series with the solenoid. In this case several such compensating coils are necessary, since there are two solenoids and two places A and D where their external effects have to be eliminated; in addition it is necessary to compensate the field within B due to C and the field within C due to B. When once this system of coils had been set up it worked quite satisfactorily and gave no trouble.

It is clear from the comparison given below that greater accuracy can be attained with cathode rays than with β-rays, arising from the fact that it is possible to produce extremely intense cathode rays and so use very narrow beams.

	β-rays	Cathode rays
Slit width	1 cm.	0·06 cm.
Radius of circular path of deflected rays...	3·5 cms.	10 cms.

Experimental Results.

Before actually giving a table illustrative of the results obtained, attention must be drawn to one or two points in connection with the measurements. When there is no screen above the slit N, magnetic deflection of the rays traversing the solenoid C reveals a sharply defined bright spot of the same width as the original undeflected one; moreover, when this spot is bent through a right angle the currents traversing B and C are both exactly the same. When, however, a thin sheet of metal is placed above N the spot when deflected is drawn out into a band showing that there are rays of all sorts of velocities in the transmitted beam; there is, however, in most cases a marked maximum which can be measured fairly easily (Fig. 2). As v_0 increases this transmitted maximum becomes more and more marked, being accompanied with less and less continuous spectrum. It might be thought, therefore, that on this account it would be best to confine measurements to the higher velocity rays; it has to be borne in mind, however, that as v_0 increases $v_0 - v_x$ becomes less, so that it

is necessary, in order to get really good measurements, to strike the medium and use a beam of incident rays fast enough to give a well-marked maximum, and yet not too fast for v_x to approach indistinguishably near to v_0 (see Fig. 2). It is possible, however, to make fairly good measurements over a range for v_0 of between 4 and 9×10^9 cms./sec., using the thinnest metal leaf as absorber.

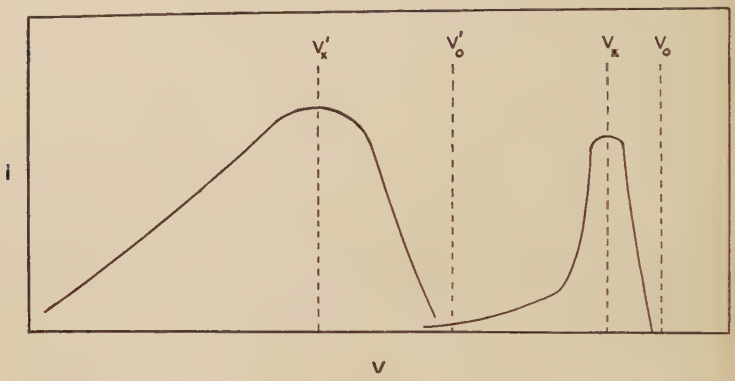


Fig. 2.

On account of the difficulty of the measurements it is usually necessary to take the mean of a large number of measurements; the necessity for this will be obvious when it is pointed out that errors in v are magnified in testing a law involving a power of v. In the following table some results using a single thickness of copper leaf are given. It is clear that $(v_0^4 - v_x^4) = \text{Constant}$.

TABLE I.

v_0	v_x	$(v_0^4 - v_x^4)$
$5{\cdot}31 \times 10^9$	$4{\cdot}59 \times 10^9$	$3{\cdot}51 \times 10^{38}$
$6{\cdot}12 \times 10^9$	$5{\cdot}72 \times 10^9$	$3{\cdot}33 \times 10^{38}$
$6{\cdot}94 \times 10^9$	$6{\cdot}66 \times 10^9$	$3{\cdot}50 \times 10^{38}$
$7{\cdot}76 \times 10^9$	$7{\cdot}53 \times 10^9$	$3{\cdot}80 \times 10^{38}$
$8{\cdot}58 \times 10^9$	$8{\cdot}45 \times 10^9$	$3{\cdot}20 \times 10^{38}$

When different thicknesses of leaf are used it appears that the formula deduced by Sir J. J. Thomson* is true:

$$v_0^4 - v_x^4 = a \,.\, x.$$

* *Conduction through Gases*, 2nd ed. p. 378.

t is not easy to test this very accurately however, for the fol-owing reason: it is necessary to use very thin leaf with cathode ays of such moderate velocities as are here used, and it is sually found that such thin sheets, while of a uniform *average* hickness from sheet to sheet, vary from point to point in the ame sheet. It is clear therefore that in order to determine the onstant a with any accuracy it is necessary to make a great many leterminations.

The constant a has been determined with some accuracy in he case of aluminium. For this metal $a = 7{\cdot}32 \times 10^{42}$.

Thus the velocity v_x of the cathode rays of initial velocity v_0 fter passing through x cms. of aluminium is given by

$$v_x = (v_0^4 - 7{\cdot}32 \times 10^{42} \times x)^{\frac{1}{4}}.$$

It is of some interest to see how this formula, which holds for athode rays moving with moderate velocities, will bear extension o the case of β-rays.

W. Wilson* has measured the diminution of velocity suffered y high-speed β-rays from radium on passing through ·0245 cms. f Al.

In the following table his results are compared with those esulting from an application of the cathode ray formula just iven.

TABLE II.

v_0	v_x (observed by Wilson)	v_x (calculated from formula)
$2{\cdot}565 \times 10^{10}$	$2{\cdot}25 \times 10^{10}$	$2{\cdot}24 \times 10^{10}$
$2{\cdot}735 \times 10^{10}$	$2{\cdot}68 \times 10^{10}$	$2{\cdot}48 \times 10^{10}$
$2{\cdot}818 \times 10^{10}$	$2{\cdot}77 \times 10^{10}$	$2{\cdot}59 \times 10^{10}$

It seems, then, that the cathode ray formula bears extension o the case of β-rays as fast as the slowest used by Wilson, since he agreement between the calculated value of v_x and the observed s less than 1 per cent.

I have to thank Sir J. J. Thomson for his kind interest in hese experiments.

* *Loc. cit.*

The Velocities of the Cathode Particles ejected by Characteristic Röntgen Radiations. By R. WHIDDINGTON, B.A., St John's College. (Communicated by Professor Sir J. J. THOMSON.)

[*Received* 5 July 1911.]

It is now well known that metal surfaces exposed to the action of Röntgen radiation emit high speed cathode rays in addition to the various kinds of secondary Röntgen rays. As a result of the researches of Innes, Cooksey and others these secondary cathode rays are known to possess the following properties:—

(1) Their velocity is independent both of the nature of the emitting metal and of the intensity of the stimulating Röntgen rays.

(2) Their velocity is largely influenced by the quality of the stimulating X-rays, harder X-rays producing faster cathode rays.

This preliminary note has to do with (2), the object being to show that by making use of the characteristic radiations of Barkla and Sadler greater precision can be given to it than would otherwise be possible.

The experiment of producing secondary cathode particles by means of characteristic radiations and directly measuring their velocity while perhaps not impossible would be extremely difficult and indeed has not yet been successfully attempted.

It is possible, however, to get some light on this question of variation of secondary cathode ray velocity with quality of X-ray from some absorption experiments carried out recently by Sadler and by Beatty. These two observers have quite independently investigated the way in which these cathode particles are absorbed by air. The interpretation of their results, however, is made difficult and rather uncertain by the fact that the coefficients they measure agree in only a few cases.

For details of these experiments reference must be made to the original papers*. In their experiments various characteristic X-radiations were made to fall on a tertiary radiator and the absorption in air of the resulting cathode rays measured. Sadler found that an exponential law of absorption fitted his results; Beatty, on the other hand, assumed it in order to express his results in terms of some easily defined coefficient. Both observers therefore seem to be measuring the same thing.

* See reference in Table I.

The coefficient λ they both tabulate occurs in the usual ormula

$$I = I_0 . e^{-\lambda . x},$$

n which I = the energy of a stream of particles of initial nergy I_0, after traversing x cms. of air.

Now Beatty calculates λ from the distance d (proportional to $1/\lambda$) in air which his cathode particles had to travel in order o dissipate half their initial energy. Thus if we regard the bsorption of these particles as due rather to energy diminution han to decrease in number we can apply the relation of the revious paper and say that

$$v_s^4 - \tfrac{1}{4} . v_s^4 = a . d$$

where v_s = the initial velocity of the particles],

i.e. $$\tfrac{3}{4} v_s^4 = a'/\lambda,$$

whence we have $$\lambda . v_s^4 = \text{Constant}^*.$$

If λ is regarded as a measure of the diminution of number of he rays the evidence so far available† goes also to show that

$$\lambda . v_s^4 = \text{Constant}.$$

A comparison of the results of Beatty and Sadler can be made easily from the following table, consisting of values of λ taken from their papers.

TABLE I.

Tertiary Radiator	Secondary Radiator								
	Fe	Cu	Zn	As	Se	Sr	Mo	Ag	Sn
Iron (S.‡)	—	37·0	35·8	30·2	26·4	21·5	15·8	8·84	6·41
Silver (B.§)	87·2	51·9	42·7	27·4	—	—	—	—	3·97
Selenium (B.‖)	—	—	—	—	—	16·1	14·0	8·8	6·5

It is clear from the above table that only in three cases (Mo, Ag, and Sn) are the two observers in good agreement.

These three values of λ are perhaps hardly sufficient to establish any law quite definitely. We see, however, that for these three types of ray the relation $\lambda w^4 = \text{Constant}$ is true to

* A more complete discussion of this and other points will be attempted in a future paper.

† Lenard, *Wied. Ann.* LVI. 1895.

‡ Sadler, *Phil. Mag.* March 1910, p. 347.

§ Beatty, *Phil. Mag.* August 1910, p. 324.

‖ Beatty, *Proc. Roy. Soc.* 1911, p. 238.

an accuracy of a few per cent., w being the atomic weight of the secondary radiator.

TABLE II.

Secondary Radiator	λ (B.)	λw^4
Mo	14·0	$1{\cdot}19 \times 10^9$
Ag	8·8	$1{\cdot}20 \times 10^9$
Sn	6·5	$1{\cdot}16 \times 10^9$

On the assumption that $\lambda v_s^4 = \text{Const.}$ we have the result that $v_s = k' . w$; that is, the velocity of a secondary cathode ray is simply proportional to the atomic weight of the radiator supplying the characteristic X-rays.

It is unfortunate that the data for the radiators of atomic weight less than Mo should be conflicting. It is to be noticed, however, that the numbers given by Sadler for the range Cu...Sr *do not lead to a law similar to that for the range Mo...Sn*; on the other hand, Beatty's results lead to the same law over the whole range.

In the following table Beatty's results are given, and the values of λw^4 calculated from them show its approximate constancy over a very great range from Fe to Sn. The fact that the numerical value of λw^4 is much less in this table than in Table II is due to the experimental differences in λ (compare λ for Sn in the two tables). A systematic source of error in either, of the right amount, would of course bring them together.

TABLE III.

Secondary Radiator	λ (B.)	λw^4
Fe	87·2	$\cdot 85 \times 10^9$
Cu	51·9	$\cdot 85 \times 10^9$
Zn	42·7	$\cdot 78 \times 10^9$
As	27·4	$\cdot 86 \times 10^9$
Sn	3·97	$\cdot 78 \times 10^9$

We thus see that Beatty's results lead to the relation

$$v_s = k' \cdot w$$

ver the whole of his range, while Sadler's results lead to this w only in the case of radiations more penetrating than that om Mo. There is no very apparent reason for these fferences.

A short time ago the writer found an experimental law of the me form as the above as a result of some work on the production characteristic Röntgen radiations*.

The experiments alluded to were carried out in the following eneral way:—

The velocity of the cathode rays within a specially designed -ray tube was gradually increased until the radiation charac-eristic of some radiator placed outside the tube in the path of he primary Röntgen beam was just excited. By using different adiators it was found that the relation

$$v_p = k \cdot w$$

eld fairly closely over the range of radiations studied.

In this formula k is a constant and v_p is the velocity of those rimary cathode rays which, striking an anticathode, emit X-rays ast hard enough to excite the radiation characteristic of an lement of atomic weight w.

Now, in practice a homogeneous beam of cathode rays does ot give rise to homogeneous X-rays, indicating that all the articles are not stopped in the same time or distance. It ollows, therefore, that the above formula refers to those cathode ays which have been arrested in a time or distance shorter han the others. It will follow from the "fluorescence law" f Barkla and Sadler that the X-rays emitted by these quickest topped particles (the hardest rays given out by the bulb) are ndistinguishable from the characteristic radiation excited by hem.

This leads to a new and convenient way of defining a haracteristic radiation:—

The radiation characteristic of an element of atomic weight w s the same as the most penetrating rays produced by impact gainst a target of a stream of cathode rays moving with velocity $_p = k \cdot w$.

Summary.

The results of the preceding discussion are included in the ollowing statement of the energy transformations occurring

* *Camb. Phil. Soc. Proc.* 1911.

between the arrest of the parent cathode rays within a Röntgen bulb and the subsequent liberation of secondary cathode rays from a distant tertiary radiator.

Primary Cathode Rays of velocity just greater than $v_p = k \cdot w$

give rise to

Primary X-rays,

which give rise to

Secondary X-rays Characteristic of element of atomic weight w,

which give rise to

Secondary Cathode Rays (from any tertiary radiator) of velocity $v_s = k' \cdot w$.

To complete these relations it will be necessary to determine the constant k' (k has already been determined)*.

I am at present engaged in experiments of this kind, producing secondary cathode particles by the radiation characteristic of Cu, and attempting to measure their velocity by magnetic deflection.

* *Loc. cit.*

A Kinematical Theorem in Radiation. By R. Hargreaves, M.A., St John's College.

[*Received* 24 May 1911.]

The application of thermodynamical methods to the radiation within a closed space gives an adiabatic relation $\theta v^{\frac{1}{3}} = \text{constant}$ connecting temperature and volume, and at the same time gives a certain form to the energy function. Change of volume involves motion of the reflecting surface of the enclosure, and reflexion at a moving surface produces alteration in wave-length. To establish what is called Wien's law of displacement, wave-lengths should be altered in the same proportion as the linear elements of the space concerned. It is the object of the present note to give the kinematical theorem needed to make this step for an enclosure of any shape. Expansion is supposed to follow the same law

$$x_t = x_0 (1 + t/T)$$

for each dimension. A statement of the thermodynamical argument is prefixed, so as to present the whole argument to the reader.

§ 1. In the equation of energy,

$$dE = \theta dS - p dv \quad \ldots\ldots\ldots\ldots\ldots\ldots (1),$$

d denotes a true differential, not merely a small quantity, and the total energy E is a function of v and θ. The relation of condition into which the entropy S does not enter is

$$\theta \frac{\partial p}{\partial \theta} - p = \frac{\partial E}{\partial v} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2).$$

The distribution of energy within the volume is taken to be uniform, so that energy-content per unit volume is $e = E/v$; pressure is taken to be $e/3$ and then the relation (2) becomes

$$\theta \frac{\partial E}{\partial \theta} - E = 3v \frac{\partial E}{\partial v} \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

The solution of this equation is

$$E = \theta F(\theta v^{\frac{1}{3}}), \text{ say } \theta F(x) \ldots\ldots\ldots\ldots\ldots\ldots (4a),$$

and $$e = \theta F(x)/v = \theta^4 F(x)/x^3 \text{ or } \theta^4 f(x), \text{ where } x = \theta v^{\frac{1}{3}} \ldots (4b).$$

The functional form of S may be connected with that occurring in E, for

$$\theta dS = dE + p dv = dE + E dv/3v$$
$$= F(x) d\theta + \theta F'(x) dx + \theta F(x) (dx/x - d\theta/\theta),$$

or
$$dS = F'(x) dx + F(x) dx/x,$$

or
$$x \frac{dS}{dx} = \frac{d}{dx} x F(x) = \frac{d}{dx} x^4 f(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots (5).$$

Thus S is a function of x only, and the condition x or $\theta v^{\frac{1}{3}}$ constant represents an adiabatic relation. In an adiabatic expansion energy is lost in virtue of mechanical work done by the pressure of radiation, and temperature falls; in the course of this change total energy varies as θ, energy-content per unit volume as θ^4.

If the same process is applied to two dimensions only, and p is written $= E/2A$ where A is area, we have

$$E = \theta F(\theta A^{\frac{1}{2}}), \text{ say } \theta F(x); \text{ and } e = \theta^3 F(x)/x^2 = \theta^3 f_2(x) \ldots (6).$$

Or again if only one dimension is taken, with $p = E/l$, we have

$$E = \theta F(\theta l), \text{ say } \theta F(x); \text{ and } e = \theta^2 F(x)/x = \theta^2 f_1(x) \ldots (7).$$

The connexion between S and F does not depend on the dimensions of the space, that between f and F does. In each case the adiabatic relation makes θ inversely proportional to a linear dimension for any process of uniform extension.

If therefore wave-length varies as a linear dimension we may write $\theta\lambda$ for $\theta v^{\frac{1}{3}}$ in the functional forms and put

$$e = \theta^4 f(\theta\lambda) \text{ or } \theta^4 f(x) \ldots\ldots\ldots\ldots\ldots (8);$$

and if $e_\lambda d\lambda$ is element of energy-content per unit volume associated with wave-lengths between λ and $\lambda + d\lambda$, then

$$e_\lambda = \frac{\partial e}{\partial \lambda} = \theta^5 f'(x) = \lambda^{-5} x^5 f'(x) \equiv \lambda^{-5}\phi(x) \ldots\ldots\ldots\ldots (9).$$

If we set out from the conception of an element $e_\lambda d\lambda$, then e is got by integration between limits, and is

$$e = \theta^4 \{f(x_2) - f(x_1)\} \text{ or } \theta^4 \{f(\lambda_2\theta) - f(\lambda_1\theta)\}.$$

The use of f with a single wave-length presumes that we are dealing with a space containing energy of one wave-length, the other method that there is a continuous range of wave-lengths. The function ϕ was introduced by Wien, later theoretical and experimental work has been in close relation with that function: possibly fF or S might prove to be more convenient as the fundamental function.

§ 2. We now consider the connexion between changes in wave-length and in linear dimensions for an expansion

$$x_t = x_0(1 + t/T),$$

confining ourselves first to the case of slow movement where t/T is small for all times considered. The perpendicular from the fixed origin (taken within the space) on a tangent plane is $lx + my + nz$, its rate of extension $(lx_0 + my_0 + nz_0)/T$, or the normal velocity is p/T; and the rate of expansion of volume $\int pdS/T = 3v/T$ accords with the linear rate.

For the change in λ due to a finite number of reflexions we ay write

$$\frac{\Delta\lambda}{\lambda} = \frac{\Sigma 2w\cos i}{V} = \frac{\Sigma 2p\cos i}{VT}.$$

he linear extension

$$\frac{\Delta L}{L} = \frac{t}{T} = \frac{Vt}{VT} = \frac{\Sigma l}{VT},$$

here L is any linear dimension and Σl the sum of lines described i the time t. Thus in order to make $\frac{\Delta L}{L} = \frac{\Delta\lambda}{\lambda}$, we require

$$\Sigma 2p\cos i = \Sigma l \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10).$$

This relation can be proved for any closed circuit in which a y returns to an original starting point. Consider first a *plane* rcuit $ABCDA$, from O draw perpendiculars OP on DA, OQ on B, OM on the reflecting surface AM, Mp on DA and Mq on AB. hen $Pp = p\cos i = Qq$ and $Ap = Aq$; and in every case

$$2p\cos i = Pp + Qq \pm (Ap - Aq).$$

he positive sign is required if P is to the rear of A in the course the ray DA, the negative if P is in advance of A. The forms ken by the result are $AP + AQ$, $AP - AQ$, and $-AP + AQ$; the gative sign occurs with AP if P is in advance of A, with AQ if is to the rear of A. The sum of corresponding elements of path ken in connexion with each reflexion is the length of the closed rcuit.

Next suppose the path not confined to a plane but still a rcuit. Let O' be the fixed origin, O its projection on the plane reflexion; OM is equal and parallel to the perpendicular from on the tangent plane at A, and the result just given is applic- le for the reflexion at A. But at B the plane of reflexion may e altered, and we have to deal with O'' the projection of O' on ie new plane of reflexion which contains the line AB. This ojection is made in the plane $O'OQ$ and the perpendicular from $''$ on the tangent plane meets AB in Q. Thus Q the forward rminal in the section of path used above is the rearward terminal the section attaching to the reflexion at B, and this is the point eeded to make the extension from plane space to space of three mensions.

The sum $\Sigma p\cos i$ is invariant for different positions of O, but if were taken outside the space, or on the far side of any reflecting irror, the corresponding perpendicular would have a negative gn; for that mirror would be approaching the ray, that is λ ould be shortened, which corresponds to a negative value of p. or the type of motion considered an expansion estimated from

one fixed point O_1 is equivalent to the expansion from another point O together with a translation of O in the line O_1O, for the multiplication of $X_0 = x_0 + \alpha$ by $1 + t/T$ gives $X = x + \alpha + \alpha t/T$, and a component of the velocity of translation of O is α/T.

§ 3. For thermodynamical application infinitely slow motion is sufficient: but the kinematical theorem is true for a finite rate of expansion, with a proof slightly modified. We are to show that $\lambda_C : \lambda_0 = L_C : L_0$ ratios referring to wave-length and any linear dimension L at beginning and end of cycle, in virtue of ratios written for each separate reflexion, of which the product is taken. In treating the reflexion at A it is necessary to consider the mirror AM in the position occupied at the moment of reflexion, and further the extension of the perpendicular from O on AM is the only motion affecting wave-length at this reflexion. If the times t_0, $t_0 + t_1$, $t_0 + t_1 + t_2$ refer to the points PAQ, and p_0, p_1, p_2 are the lengths of the perpendicular at these times, or $p_1 = \varpi\,(1 + t_0/T)$, ..., then with $\varpi/T = w$ we have $p_1 - p_0 = wt_1$, $p_2 - p_1 = wt_2$. Hence $p_2 : p_0 = p_1 + wt_2 : p_1 - wt_1$ is the ratio of *any* linear elements at times t_0 and $t_0 + t_1 + t_2$, expressed in terms of the perpendicular at the moment of reflexion and the velocity affecting wave-length. As $AP = Vt_1$, $AQ = Vt_2$ we require

$$\lambda' : \lambda = Vp_1 + wAQ : Vp_1 - wAP \quad \ldots\ldots\ldots\ldots (11)$$

to be a consequence of the exact law of reflexion. This law is

$$\sin i' : \sin i = V\cos i' + w : V\cos i - w$$
$$= V + w\cos i' : V - w\cos i = \lambda' : \lambda \quad \ldots\ldots (12).$$

But if x is the perpendicular from O on the normal at A,

$$AP = p_1\cos i - x\sin i, \quad AQ = p_1\cos i' + x\sin i',$$

and therefore

$$Vp_1 + wAQ = p_1(V + w\cos i') + wx\sin i',$$
$$Vp_1 - wAP = p_1(V - w\cos i) + wx\sin i.$$

It is at once seen that (11) is satisfied in virtue of (12). The formula (11) is written for a position of O which places Q in advance of A and P to the rear of A in the course of the ray in the respective lines; the sign of AP must be reversed when P is in advance of A, that of AQ when Q is to the rear of A. The result reduces to that given above when w is small and i' is taken equal to i.

The position for a spherical enclosure is simpler because a single configuration is constantly repeated. Thus with O as centre OQ perpendicular on a chord AB representing a ray, OP on the ray incident at A, the ratio

$$OQ : OP = \sin i' : \sin i = \lambda' : \lambda.$$

The lines OP and OQ are not in one direction but they have corresponding positions in successive configurations, and their ratio may be taken as representative. But we may also take $OB : OA$ as the ratio. Thus with $OA = a_1$, $OB = a_2 = a_1 + wt$, the triangle OAB gives

$$(a_1 + wt)^2 = V^2 t^2 - 2Vta_1 \cos i' + a_1^2,$$

or
$$t = 2a_1 \frac{V \cos i' + w}{V^2 - w^2} = \frac{2a_1 (V \cos i - w)}{V^2 - 2Vw \cos i + w^2};$$

and
$$a_2 = a_1 + wt = \frac{a_1 (V^2 - w^2)}{V^2 - 2Vw \cos i + w^2},$$

while
$$\frac{\lambda'}{\lambda} = \frac{V + w \cos i'}{V - w \cos i} = \frac{V^2 - w^2}{V^2 - 2Vw \cos i + w^2}, \text{ and } \frac{a_2}{a_1} = \frac{\lambda'}{\lambda}.$$

The time from A to B is not the same as from P to Q. To find the angle OBA or i_2, the next angle of incidence, we have

$$a_1^2 = V^2 t^2 + (a_1 + wt)^2 - 2Vt (a + wt) \cos i_2,$$

or
$$t (V^2 - 2Vw \cos i_2 + w^2) = 2a_1 (V \cos i_2 - w),$$

which on comparison with the previous value in terms of $\cos i$ gives $i_2 = i$, that is angles of incidence and reflexion are repeated. The angle at the centre is given by

$$1 + \cos AOB = 2V^2 \sin^2 i / (V^2 - 2Vw \cos i + w^2).$$

What is the significance of the circuit in this connexion? Two events are to be connected, an expansion proceeding continuously and a reflexion-effect occurring at intervals, not necessarily equal. For small motions each reflexion-effect corresponds to the expansion during a definite interval of time. If there is a cycle the total reflexion-effect in the cycle agrees with the expansion in the period of the circuit, and there is no element of indefiniteness. If there is no cycle, there still exists an exact correspondence between the two effects, provided the choice of points for start and terminus of time is made for any group of reflexions as in the theorem. At times corresponding to positions between the perpendiculars, now one now the other effect may be in excess, in the long run they agree. Thus, for the purpose of application to Wien's law of displacement, the distinction between rays following cyclic and acyclic paths appears to be of little moment.

A Study of the Radium Emanation contained in the air of various soils. By JOHN SATTERLY, D.Sc. (Lond.), M.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 26 July 1911.]

In previous papers* the author has published results obtained for the amount of radium emanation contained in the air and in certain waters. Since the source of all this emanation is the emanation given off by the radium in the soil it was thought advisable to conclude this research by a study of the emanation-content of the air that could be withdrawn from the soil. The actual radium-content of various rocks and soils has been measured by many observers and has been found to be about $1{\cdot}4 \times 10^{-12}$ gm. of radium per gm. of rock. The results of the experiments described below show that only about one-seventh of this amount is required to supply the emanation that can be withdrawn from the ground by suction; the rest of the emanation is evidently occluded and dies where it was born.

The paper is divided into the following sections.

(1) Preliminary experiments.
(2) Description of the two series of experiments.
(3) Pipe-experiments:
  (*a*) Pipes going to different depths in the same soil.
  (*b*) Effect of a continual withdrawal of air.
  (*c*) Pipes going to the same depths in different soils and observed at different times under different weather conditions.
(4) Bottle-experiments with different soils.
(5) Comparison of the results with the two methods of experiment.
(6) Search for a relation between the emanation-content of the air and the weather.
(7) Comparison of the emanation-content of ground-air and atmospheric-air.

The testing apparatus was the same as that used in my previous experiments on radium emanation.

All the experiments were made in the afternoon between the hours of 2 and 6.

(1) *Preliminary experiments.*

A "compo" pipe about $\frac{1}{2}$ cm. in bore was connected at one end to an open wooden box and this was placed at the bottom of a pit 120 cms. deep dug into the soil of the garden border outside the laboratory window. The pit was then filled up and the soil

* *Phil. Mag.* Oct. 1908 and July 1910; *Proc. Camb. Phil. Soc.* Vol. xv, Pt vi.

ently pressed around the pipe. The position of this pipe is narked *A* in Fig. 2.

At first before knowledge was obtained of the enormous mount of emanation that could be withdrawn from the soil this ipe was connected up in series with a tube containing charcoal*, gauge and a water pump and air drawn through at ½ litre er min. for 21 hours. On testing in the usual way† a leak f from 400—1000 cms. per minute on the electrometer scale was btained, whereas if the atmospheric-air had been under test a eak of about 2—3 cms. per minute might have been obtained. horter exposures gave even a higher emanation-content for the r from the soil and it was evident that the charcoal was getting turated and also that it was not necessary to use a charcoal tube t all: the air from the soil could be passed straightway into the sting vessel.

Tests were therefore made as follows: The testing vessel was khausted as much as possible by the water-pump (usually to bout 2 cms. of mercury). Meanwhile air was drawn through the round-pipe by another pump for 10 mins. at the rate of ½ litre er min. This cleared out all air left in the ground-pipe itself om the last observation. The testing vessel was then connected rough a drying-tube to the ground-pipe and filled slowly with ie air from the ground. Leaks taken immediately after the lling always showed the presence of thorium emanation. After 0 mins. this would decay practically to zero and the reading was hen taken of the amount of radium emanation present.

The table on p. 338 shows the variation during about three eeks of the emanation obtained from the soil in this way. When o remark is made in the last column the procedure of testing as as described above, in other cases the remarks indicate how is procedure was modified. The second, third and fourth olumns give an idea of the weather changes occurring during ie time. There was little wind or rain during this set of xperiments.

In all cases the amounts of emanation are quoted in terms f the leaks obtained per minute, the leaks being corrected to common sensitiveness of the electrometer (900 mm. per volt), nd the air leak (which varied on different days from ·9 to 1·3 cms. er minute), subtracted.

It may be remarked that previous experiments‡ had shown

* See *Phil. Mag.* July 1910, p. 1.

† The electrical apparatus used was the same as that described in *Phil. Mag.* t. 1908 and July 1910. See also Fig. 4 of this paper, where *V* is the testing ssel charged to 320 volts by a wire *C*, *W* is the insulated wire connected to an ectrometer at *Q*, *E* is the earth wire of the guard ring and *M* a mercury anometer.

‡ *Proc. Camb. Phil. Soc.* Vol. xv. Pt vi.

that a leak of 1 cm. per minute corresponds to an amount of emanation that would be produced by 78×10^{-12} gm. of radium in

Date, 1911	Weather	Bar.	Max. Temp.	Min. Temp.	Leak due to emanation withdrawn
Jan. 17	Overcast	779	45	26	17·3 (rising to 25·0 in 3 hrs.) *
,, 18	,,	779	43	39	19·4. After another 90 litres drawn through, 20·8
,, 19	,,	777	41	35	After 300 litres drawn through, 18·4
,, 20	,,	775	37	30	After 720 litres drawn through, 9·7. After a 3 hrs' wait, 8·2
,, 21	,,	767	37	35	No air previously drawn through, 14·5
,, 22	,,	767	41	36	
,, 23	,,	767	42	30	11·1
,, 24	Sunny	767	48	31	19·1
,, 25	Clear	765	50	42	24·1
,, 26	Fine	769	55	42	16·4
,, 27	Overcast	770	47	42	25·9
,, 28	Fine	771	52	31	15·6
,, 29	,,	771	40	25	
,, 30	,,	770	42	32	No air previously drawn through, 4·4. After an hour's wait, 4·6
,, 31	,,	779	36	26	No air previously drawn through, 3·6. After an hour's wait, 4·2
Feb. 1	4 hrs. sun	779	37	16	8·1
,, 2	Overcast	777	35	18	11·4. After a 3 hours' wait, 12·6
,, 3	,,	774	43	32	13·3
,, 4	,,	774	43	37	
,, 5	,,	772	42	37	
,, 6	,,	774	38	34	
,, 7	3 hrs. sun	774	42	32	17·0
,, 8	Overcast	774	40	36	8 litres drawn through but no test made
,, 9	,,	770	37	33	
,, 10	,,	760	41	37	5·0

* This rise from 17·3 to 25·0 in 3 hours proves that the active gas is reall radium emanation.

ne day or the amount that would be in equilibrium with 3×10^{-12} gm. of radium.

There are great irregularities in the readings. It was hoped hat a continued frost would set in to lock up all the interstices in he upper layer of soil but the maximum temperature during the lay never fell below 32°, though on five successive days Jan. 30—Feb. 3 the minimum temperature was not above 32°, and on the arly mornings of Feb. 1 and 2 fell to 16° and 18°. The low eadings of Jan. 30 and 31, however, occurred before this hard rost.

(2) *The two series of experiments.*

It was now decided to carry out two series of experiments. n one series pipes were inserted in the same soil to different depths and in different soils to the same depth and air withdrawn by suction at different times and tested. This series will be called the Pipe-series of experiments. In the other series different samples of earth or soil were placed in bottles and the emanation that accumulated in various times was withdrawn by suction and measured. This may be called the Bottle-series of experiments.

(3) *The Pipe-series of experiments.*

The pipes used were made of narrow compo tubing of about 3 mm. bore, each pipe being 6 metres long. One end of the pipe *P* (Fig. 1) was joined to a piece of brass tubing *T*, $1\frac{1}{2}$ in. diam. and 3 in. long, the other end of the brass being closed by wire gauze to permit the entry of air. A blank experiment was made on the compo tubing to see that it was not contaminated with radioactive matter. Holes were rammed in the ground with a large crowbar or iron pipe to the depth required. The brass vessel and pipe were then lowered to the bottom of the hole. The hole was now half filled with earth and the earth rammed home. The next foot or so of the hole was filled with thick mud. It was hoped that this would set as a kind of cement and so refuse passage of air along the line of the pipe to the cage at the bottom.

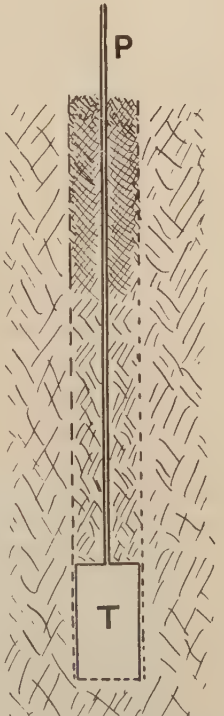


Fig. 1.

(3*a*) *Pipes going to different depths.*

Three pipes like the above were inserted to depths of 76, 152 and 229 cms. into the lawn outside the window of the laboratory and the upper ends of the pipes were brought through the window to the laboratory bench. The plan of the positions of the pipes is given in Fig. 2, the pipes being *B, C, D* respectively, *A* referring to the pipe used in the preliminary experiments.

In taking these readings the testing vessel and drying tube were exhausted by the pump as far as possible, and the drying tube was then connected to the ground-pipe, no air having been drawn previously through the pipe. The testing vessel was then slowly filled with the ground-air. The order in which the pipes were tested on any particular day is indicated by the letters *a, b, c.*

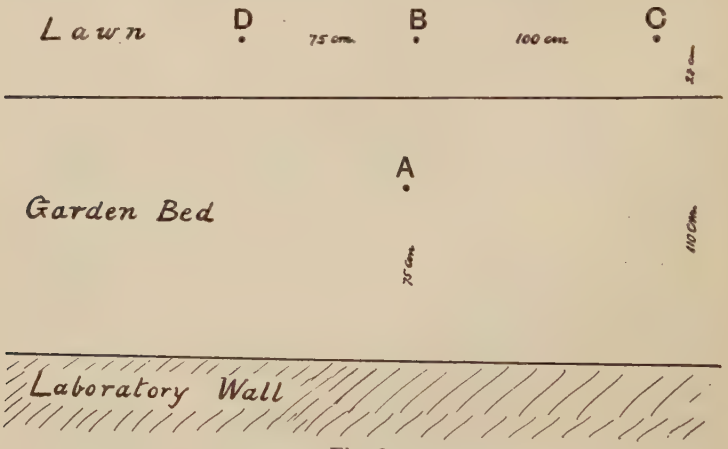


Fig. 2.

About $1\frac{1}{2}$—2 hours elapsed between the successive fillings. This long interval is necessary on account of the active deposit left in the testing vessel.

The deepest pipe always gave the largest amount of emanation and with one exception (Feb. 20) the shallowest pipe the least.

The results are given in the table on p. 341. The means of the columns are 27, 38, 60, *i.e.* in the ratio of 2 : 3 : 5, while the depths of the pipes are as 1 : 2 : 3. It is difficult to say where exactly the air was located before sucked up any pipe as we have little knowledge of the volume and distribution of the interstices of the soil.

It is worth recording that most thorium emanation was found in the air from the shallowest pipe.

Emanation obtained from pipes going to different depths.

(Volume of air drawn up = 3 litres.)

Date	*B*, 76 cms. deep	*C*, 152 cms. deep	*D*, 229 cms. deep
Feb. 2 (pipes	inserted)		
Feb. 6	*c* 37	*b* 38	*a* 45
„ 9	*a* 28	*b* 42	*c* 51
„ 13	*a* 35	*c* 42	*b* 53
„ 20	*a* 23	*c* 16	*b* 41
„ 27	*a* 19	*c* 27	*b* 47
July 18	*a* 31	*c* 43	*b* 99
„ 23	*a* 17	*c* 59	*b* 82

(3*b*) *Can the supply of emanation in the soil be exhausted by continual withdrawal?*

To test this some experiments were made with the deepest pipe *D*.

On Feb. 28th, the vessel was filled in the usual way from this pipe at 2·55 p.m. The reading was 54

From 3 h.—5½ h. air was drawn through the pipe at ·5 litre per min. and at 5½ h. the vessel was again filled. The leak was again 54

The pump was then set drawing air through the tube all night from 5⅔ h. on Feb. 28th to 2⅔ h. on Mar. 1st, when the leak was 44

The pump was set in action again until 5⅓ h. when the leak was 43

After another all night running the leak at 2.50 on Mar. 2nd was 45

And again after another all night running the leak at 2.50 on March 3rd was 47

The result from this is that although the leak during a constant running of the air through the pipe is not as great as it is after say a day's rest, yet the supply of emanation is very considerable and approximates to a constant quantity, in the above case about ⅚ths of the maximum amount that can be got out of the soil. Similar results are shown in the table on p. 346, obtained with pipe *C*.

(3*c*) *Pipes inserted into different soils.*

In this series of experiments the air had to be withdrawn from the pipe and taken to the laboratory. The method of withdrawal was water-suction. A bottle *B* (Fig. 3) of volume just larger than that of the testing vessel was provided with two taps one at the top and the other at the bottom. The bottle was filled with distilled water and taken out to the pipe. The upper tap was then connected to the ground-pipe *P*, and the lower one to a length (7 ft.) of compo tubing *M*. The bottle was supported so that this compo tubing rested in an oblique position and when both taps were turned the water escaped through *M* and the fall of water so produced sucked the air up *P*. When all the water had run out the taps were closed and the ground-pipe detached from the bottle and sealed again to wait for the next reading.

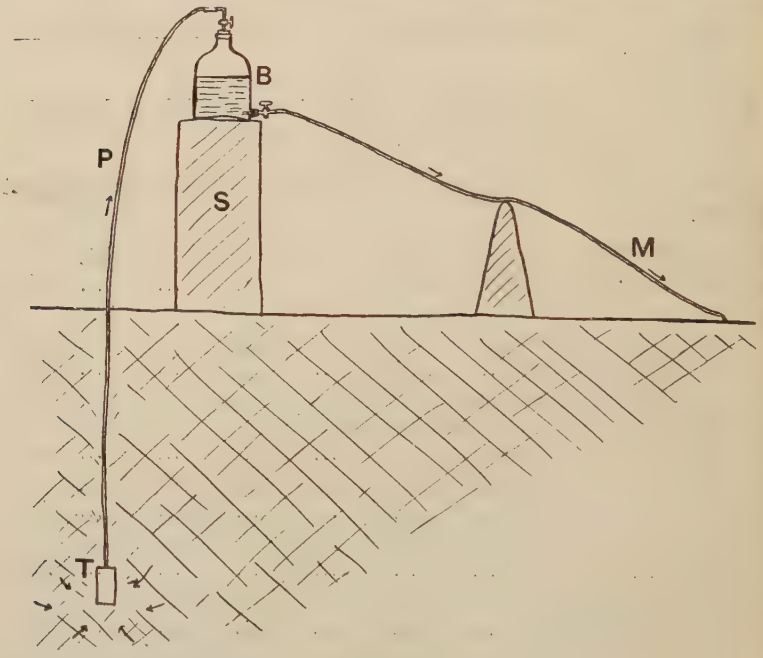


Fig. 3.

The time the bottle took to empty was nearly always noted, it being a guide to the porosity of the soil (the same fall-tube was used in all cases except where otherwise mentioned). On reaching the laboratory the testing vessel was exhausted and then filled with the air thus collected and the usual measurements taken.

(1) *Pipe in the Chalk at the Cherryhinton Pit.*

A pipe was inserted in a hole 106 cms. deep in a large bank of rather loose chalk that had been quarried some years ago and then thrown on one side as being too small for burning. The bank is now scantily covered with vegetation. When the pipe was inserted the hole was sealed in the usual way. The results are expressed in the following table.

Date	Weather remarks	Bar.	Temperature		Rain in inches	Time in minutes occupied in collection	Emanation content
			Max.	Min.			
Mar. 4	Fine. Pipe inserted						
,, 4–8	Sunny. Rain at times	—	—	—	·13	—	—
,, 8	Gloomy	764	47	28	—	30	18
,, 8–16	Snow. Rain each day	—	—	—	·99	—	—
,, 16	Unsettled. Snow. Rain	752	46	31	·04	not taken	7
,,16–21	At first fine, then dull	—	—	—	—	—	—
,, 21	Dull morning. Glorious afternoon	757	54	35	—	not taken	7
,,23–31	Little snow. Gloomy	—	—	—	·08	—	—
,, 31	Gloomy	757	50	42	—	20	21
Apr. 7–25	Fine. Sunny. Scarcely any rain	—	—	—	·05	—	—
,, 25	Glorious	758	59	47	—	17	19
May 15–June 2	Glorious weather. Hot	—	—	—	—	—	—
,, 2	Very hot	765	76	47	—	19	19
,,23–26	Much rain at times	—	—	—	1·27	—	—
,, 27	Dull morning. Fine afternoon	768	72	48	—	20	18
Aug. 16	Fine since June 26th	768	73	51	—	19	9
Sept. 23–29	Unsettled. Occasional rain	—	—	—	·50	—	—
,, 30	Unsettled. Windy. Wet	756	58	45	·21	24	12
Oct. 1–23	Unsettled. Occasional rain	—	—	—	1·50	—	—
,, 24	Raining	747	56	46	·1	22	21

The emanation-content was remarkably constant from the end of March to the end of June. There seems however no possibility of correlating emanation-content with the weather, for the high and low results are apparently indiscriminately scattered over fine and wet weather.

(2) *Pipe at the Observatory.*

By permission of Sir Robert Ball and with the help of Mr Hinks a pipe was inserted 106 cms. deep through the upper soil of leaf mould into the clay just inside the grounds of the Observatory. Repeated attempts to suck air up the pipe with the water bottle failed and even when a vacuum was applied only a spurt of watery mud resulted. The pipe was waterlogged in the clay and it was therefore abandoned. Another hole was made at a higher level but even here at a depth of 84 cms. water was reached, so the hole was filled up with gravel for about 6 cms. and the pipe then inserted. Results:

Date	Weather remarks	Bar.	Temperature		Rain in inches	Time in minutes occupied in collection	Emanation content
			Max.	Min.			
Mar. 14	Wind. Snow. Hail. Inserted pipe						
,, 16–20	Dry (·25 in. rain on 15th)	—	—	—	—	—	—
,, 20	Glorious	756	53	37	—	not taken	47
,, 20–28	·17 in. rain on 21st. Snow storms	—	—	—	·30	—	—
,, 28	Sunny. Fine. Windy	758	53	34	—	16	52
Apr. 24	Scarcely any rain for a month	761	64	43	—	17	76
May 14-17	14th, rain. 15th, dull. 16th, 17th, fine	—	—	—	·67	—	—
,, 18	Dull. Cold.	762	58	47	—	not taken	43
June 2	Very hot. No rain since May 14	765	76	47	—	16	25
,, 23–26	Much rain on June 24	—	—	—	1·27	—	—
,, 27	Dull morning. Fine afternoon	768	72	48	—	18	41
July 12	Hot for the last week	775	78	53	—	not taken	34
Aug. 15	Hot for the last 6 weeks	768	70	54	—	19	28
Sept. 23–29	Unsettled. Occasional rain	—	—	—	·50	—	—
,, 30	Unsettled. Windy. Wet	761	58	45	·21	19½	53
Oct. 1–23	Unsettled. Occasional rain	—	—	—	1·50	—	—
,, 24	Raining	747	56	46	·1	21	64

The highest result (April 24) here was obtained after a spell of fine weather, so also was the lowest result (June 2). It seems impossible to correlate weather and emanation-content in this case.

(3) *Pipe in a lawn in the town of Cambridge.*

A pipe was inserted to a depth of 106 cms. in the middle of a lawn. The soil immediately underneath the turf contains much builder's rubbish but lower down gravel and drift most likely occur. Results:

Date	Weather remarks	Bar.	Temperature		Rain in inches	Time in minutes occupied in collection	Emanation content
			Max.	Min.			
Mar. 4	Fine. Pipe inserted						
,, 6–7	Dull	—	—	—	·03	—	—
,, 8	Dull	763	47	28	—	not taken	23
,, 12–14	Wind. Hail. Snow. Rain	—	—	—	·50	—	—
,, 15	Snow. Rain. Raining during filling of bottle	746	41	32	·25	120	17
,, 17–20	Windy. Sunny. Fine	—	—	—	—	—	—
,, 21	Dull morning, then glorious	756	54	35	—	45	83
,, 26–28	Windy. Sunny. Fine	—	—	—	·05	—	—
,, 29	Dull	759	47	40	—	37	78
Apr. 25	Glorious. No rain for 3 weeks	759	59	47	—	20	14
May 30	Hot and dry for some time	762	74	50	—	23	13
Jun. 23–26	Lot of rain at times	—	—	—	1·27	—	—
,, 26	Dull	769	58	50	—	22	83
July 1–4	Fine weather	—	—	—	·07	—	—
,, 5	Fine	770	76	53	—	25	74
,, 13	Fine for a fortnight	775	77	50	—	23	60
Aug. 14	Fine for 6 weeks	768	84	57	—	27	59
Sept. 23–29	Unsettled. Occasional rain	—	—	—	·50	—	—
,, 30	Unsettled. Windy. Wet	762	58	45	·21	22½	63
Oct. 1–22	Unsettled. Occasional rain	—	—	—	1·50	—	—
,, 23	Dry; ·4 in. rain on 21st and 22nd	753	59	50	—	22	76

Here again it seems impossible to obtain any relationship between the emanation-content and any of the weather factors.

(4) *Pipe in the Court of the Cavendish Laboratory.*

Readings were taken with the 152 cm. pipe mentioned above. Up to April 24 the fall tube attached to the water bottle was a wide indiarubber tube. After that date the 7 ft. compo tube was used.

Date	Weather and other remarks	Bar.	Temperature		Rain in inches	Time in minutes occupied in collection	Emanation content
			Max.	Min.			
Mar. 13	12th and 13th. Wind. Rain. Hail	748	43	33	·42	10½	25
,, 15	14th and 15th. Wind. Rain. Hail	746	41	32	·33	30	24
,, 20	17th to 20th. Fine and sunny	756	53	37	—	8	43
,, 27	25th to 27th. Snow. Cold. Windy	760	39	36	·05	5	27
Apr. 24	Fine for a month. Warm	761	64	43	—	4	24
Apr. 25–May 2	Sunshine and rain	—	—	—	·67	—	—
May 3	Windy	756	56	39	—	not taken	21
,, 4	Pump drew air through all night at ½ litre per minute. Stopped just before filling the bottle	760	61	38	·07	not taken	30
,, 16	14th, Very wet (·67 in.). 15th and 16th, Dull	757	70	43	—	23	57
,, 17	Fine	759	70	47	—	23	70
,, 18	Dull } Pump on all night. Just stopped it to	764	58	47	—	24	70
,, 19	Dull } fill the bottle	763	56	42	·02	24	69
,, 23	20th and 21st, Cold, dull. 22nd and 23rd, Fine	761	68	44	—	25	39
,, 24	Fair	762	69	54	—	25	27
,, 29	25th–28th, Fine. 29th, Hot	765	78	51	—	23	67
,, 30	Pump on all night. Hot	761	74	50	—	—	—
,, 31	,, ,, ,,	760	76	51	—	30	72
June 1	,, ,, ,,	765	81	52	—	23	72
,, 2	,, ,, ,,	764	76	47	—	25	75
,, 6	2nd–6th. Hot	774	75	54	—	25	75
,, 13	7th–12th, Fine. 13th, Cool	759	60	47	—	not taken	61
,, 19	16th–18th, Rain (·32 in.) at intervals. 19th, Wet	753	64	52	·03	24	37
	Repeat after 2 hours' rest	—	—	—	—	not taken	37
,, 20	Lot of rain on night of 19th	761	68	53	·56	25	32
,, 21	Dull, cool	763	69	52	—	25	30

Date	Weather and other remarks	Bar.	Temperature		Rain in inches	Time in minutes occupied in collection	Emanation content
			Max.	Min.			
June 24	22nd, Dull. 23rd and 24th, Lot of rain	749	64	53	·9	25	21
,, 25	Still raining	755	55	51	·14	25½	22
,, 28	Little rain in the night	768	72	48	—	26	23
July 5	After 4 or 5 days' fine	773	76	53	—	26	56
,, 6	Hot	768	84	59	—	26	70
,, 7	,,	770	81	53	—	26	72
,, 10	Hot on 8th, 9th and 10th	775	70	49	—	27	78
,, 11	Hot	777	76	47	—	25	76
,, 12	,,	775	78	53	—	26	72
,, 13	,,	775	77	50	—	26	78
,, 26	Rain and Thunder-storm 6—10 a.m.	760	75	55	·23	26	59
	Reading at 2.30 p.m.					25	63
,, ,,	Repeated at 5.30						
,, 28	Hot	763	88	57	—	24	66
Aug. 3	Hot for days	763	76	59	·01	25	38
,, 4	,, ,, ,,	764	77	54	—	25	37
,, 10	Hose turned on grass for 1½ hrs	767	77	56	—	24½	54
,, ,,	Readings before and afterwards					24½	52
,, 21	Raining since 4½ h. a.m. reading at 10 o'cl.	753	69	61	·24	24	54
,, ,,	reading at 6 o'cl.					24	56
,, 22	Rain in night. Hose turned on from 2.30 —7.15	756	65	58	·19	24	62
,, ,,	Readings before and after					25½	60
Sept. 23–29	Unsettled. Occasional rain	—	—	—	·50	—	—
,, 30	Unsettled. Windy. Wet	756	58	45	·21	26	30
Oct. 1–5	Fairly dry	—	—	—	·27	—	—
,, 6	Sunny, warmer	764	58	48	—	27	65
,, 13–16	Gloomy. Wet	—	—	—	·36	—	—
,, 16	Gloomy. Drizzling	768	53	50	·03	27	55
,, 19–23	Dull. Wet	—	—	—	·55	—	—
,, 23	Dull	753	59	50	·16	28	15
,, 25	·36 in. rain on night of 24th	745	59	46	·36	27	30

In this case there are a few indications that fine hot weather causes an increase in the emanation-content and rain a decrease. Increases which accord with this occurred on Mar. 20, May 16, 29,

July 5 and decreases in agreement on Mar. 27, June 19, 24, Sept. 30.

In two cases, Aug. 10 and 22, the grass was flooded with water for some hours but little effect was produced. Cambridge tap water, however, contains much dissolved emanation and one effect may have neutralised the other.

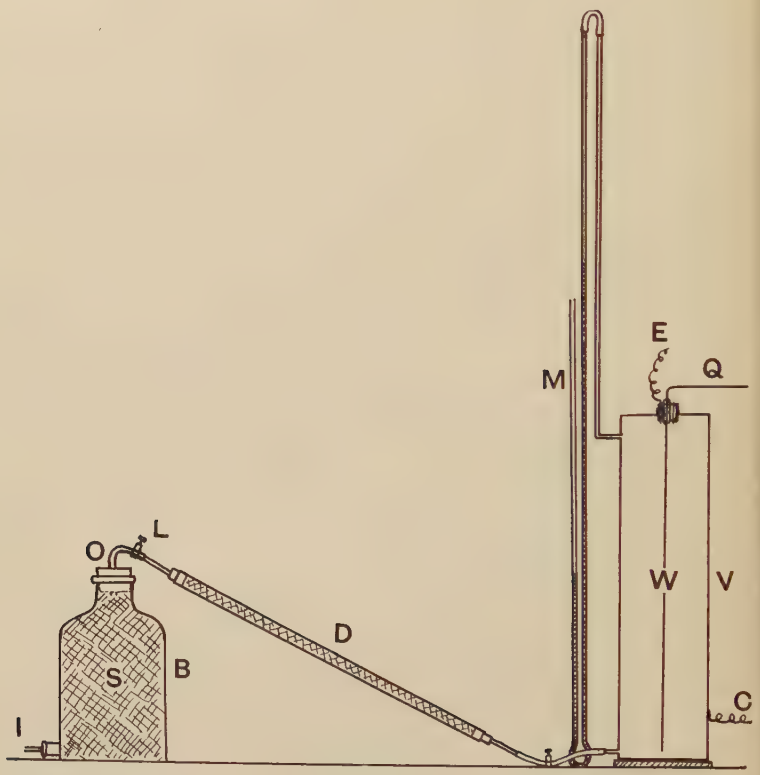


Fig. 4.

(4) *The Bottle series of experiments.*

In these experiments a bottle B (Fig. 4) was filled with a weighed quantity of soil, gault, or chalk S as the case might be. The bottle was provided with two openings I and O to allow of the admittance and withdrawal of air. The method of testing was as follows: After filling the bottle with the earth it was exhausted with the water-pump once or twice to clear out all

emanation, then filled with air, and the tubes sealed. At subsequent dates the emanation generated and mixed with the air was removed and tested. To do this the testing vessel V and its drying tube D were first exhausted as far as possible with the pump and the clip L tightened. The tube I being closed O was connected through D to the vessel and communication opened between the B and V by loosening L. The air in the bottle expanded and some rushed into the testing vessel. L was then tightened and I opened to the air thus filling the bottle again up to atmospheric pressure. Again I was shut and L opened thus sending a further quantity of emanation into the testing vessel. This was repeated two or three times. The pressure-falls (read by the manometer M) consequent on the successive connections of the bottle to the vessel give an indication of the relative volumes of the air space in the bottle and that of the testing vessel. Finally I and L were opened at the same time and the remaining traces of emanation swept out by the air rushing through the bottle to the vessel. The leak was taken immediately and also at the 10-minute maximum. Only the latter is given in the tables. The bottle was then sealed up again till the next reading.

(1) *Chalk.*

A quantity of loose chalk was taken from the bank in which the pipe was inserted. The chalk was quite damp. A bottle of volume 3500 cc. was filled with some of this on Mar. 23. Weight of chalk taken, in its damp state, = 3945 gm.

The following is an average set of pressure readings taken during the filling of the testing vessel (the procedure is described above): Barometric height, 762 mm.; vessel exhausted to 13 mm.; pressures after 1st, 2nd, 3rd fillings 269, 436 and 546 mm. respectively. The volume of the testing vessel and drying tube was 3070 cc. These pressure readings corresponded to an air space

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
Mar. 23	(bottle filled)	—	—
„ 30	5·0	7	1·2
Apr. 27	7·6	28	1·3
„ 28	1·3	1	1·3
May 1	3·0	3	1·2
July 10	7·1	70	1·2
			Mean 1·25

of 1500 cc. in the bottle. The table (p. 349) gives the results obtained. The numbers obtained in the last column are calculated from those given in the second and third columns by the use of factors obtained from the growth-curve of radium-emanation.

At the conclusion of these experiments the bottle was filled with water to find the volume of the air space; 1410 cc. of water were required; this agrees fairly well with the result obtained above; the mean is 1450 cc. The chalk was then removed and dried on an iron plate over a burner. Its weight when dry was 3160 gm. A fresh bottle, of volume 4090 cc., was now filled with this 3160 gm. plus 920 gm. of dried chalk from the same source, total 4080 gm.

Readings taken with this bottle:

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
July 25	(bottle filled)	—	—
„ 31	3·47	6	·93
Aug. 8	4·5	8	·96
			Mean 1·0(nearly)

The volume of the air-spaces calculated from the pressure readings was 2690 cc., and by filling with water afterwards 2900 cc. mean 2800 cc.

The mean daily accumulation of 1·0 requires for its production $1{\cdot}0 \times 78 \times 10^{-12}$ gm. of radium. This equals $\cdot 019 \times 10^{-12}$ gm. radium per gm. of dry chalk.

The mean daily accumulation of 1·25 obtained with the damp chalk requires for its production $1{\cdot}25 \times 78 \times 10^{-12}$ gm. of radium or $\cdot 031 \times 10^{-12}$ gm. radium per gm. of chalk (weighed when dry). The presence of the water thus increased the output of emanation. Strutt* found that different parts of this particular chalk pit differed in radium-content from the upper part containing $\cdot 2 \times 10^{-12}$ and the lower part $\cdot 4 \times 10^{-12}$ gm. per gm. Taking a mean of $\cdot 2$ it follows that my method of withdrawal removes only $\frac{1}{8}$th of the emanation generated in damp chalk and $\frac{1}{12}$th of the emanation generated in dry chalk, the remainder being locked up in the chalk.

* *Proc. Roy. Soc.*, 77 A, 78 A, 1905, 1906, corrected by Eve, *Phil. Mag.* Aug. 1907.

(2) *Earth and Gravel from the Court of the Cavendish Laboratory.*

This was taken up in a damp condition and a bottle of volume 2050 cc. filled with 2355 gm. (found afterwards to weigh 1980 gm. when dried). An average set of pressure readings during the filling of the testing vessel were: bar. 759 mm. and pressure in vessel 742, 562, 430, 322 mm. after exhaustion and 1st, 2nd, and 3rd fillings respectively. These corresponded to an air space of about 900 cc. in the bottle. Results:

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
Mar. 18	(bottle filled)	—	—
„ 30	25·5	12	4·8
May 1	27·0	31	4·6
„ 2	7·4	1	7·4
„ 3	6·1	1	6·1
„ 8	17·8	5	5·0
„ 9	6·8	1	6·8
June 12	27·8	34	4·7
„ 14	10·8	2	6·0
„ 15	5·7	1	5·7
„ 16	4·7	1	4·7
July 14	24·0	28	4·1
17	11·1	3	4·5

The results here are rather inconstant. The long rests give mean of 4·6 for the daily accumulation, but actual day's rests ive much higher results. The contents of the bottle looked ather dry on June 15th, and a considerable quantity of distilled ater was added to thoroughly damp it. This may have been he cause of the low results of June 15, 16 and July 14. Taking he mean daily accumulation as 4·6 this would be supplied by 1.9×10^{-12} gm. radium per gm. of gravel whereas the actual radium-ontent is probably about 5 or 6 times this.

At the completion of these results the earth was removed om the bottle and dried over a burner. It was then reduced to coarse powder and fairly tightly packed into a smaller bottle hich it just filled. Weight of earth, 1980 gm. Volume of ottle, 1710 c.c. Volume of air spaces, by pressure, 1000 cc.; by lling with water afterwards, 800 cc. mean 900 cc. The follow-g results were obtained with this bottle:

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
July 20	(bottle filled)	—	—
,, 25	13·2	5	3·7
Aug. 2	17·0	8	3·7
			Mean 3·7

Another bottle was filled with some more of this earth which had got dry by lying about in the laboratory during the summer. This was also coarsely powdered. Weight of earth 1450 gm. Volume of bottle 1210 cc. Volume of air spaces, by pressure, 670 cc.; by filling with water afterwards 600 cc. mean 635 cc. Results with this bottle:

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
July 17	(bottle filled)	—	—
,, 19	6·2	2	3·2
,, 25	10·2	6	2·6
Aug. 2	12·3	8	2·7
,, 15	15·3	13	2·6
			Mean 2·8

Both the 3·7 for the 1980 gm. and the 2·8 for the 1450 gm. correspond to a radium content of $\cdot 15 \times 10^{-12}$ gm. per gm. of earth: so that in this case also the presence of water increased the emanation output, but not to such an extent as in the case of the chalk.

(3) *Gault.*

The gault is a stiff lead-blue clay, impervious to water. It underlies the town of Cambridge and is much used for making bricks. The specimen used was taken off the workman's spade during digging operations in the Newmarket Road pit. It was of the consistency of butter (in winter) and to get plenty of surface exposed it was chiselled into shavings and fragments not larger than kidney-beans. As a check on each other and a test of the accuracy of working, two bottles of about the same size were filled. (1) contained 1800 gm., (2) contained 1920 gm. An average set of pressure readings with (1) was: bar. height = 762 mm

Pressure in vessel = 15, 164, 297, 393 mm. after exhaustion and 1st, 2nd, and 3rd fillings respectively, whence volume of air in (1) = 750 cc. The volume of air-space determined by water filling afterwards was 720 cc. There was the same volume in (2). Results:

(1)

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
May 12	(bottle filled)	—	—
„ 15	9·1	3	3·6
„ 22	14·7	7	3·4
„ 26	9·7	4	3·2
July 10	16·4	45	2·8
„ 14	9·1	4	3·0
			Mean 3·2

(2)

May 12	(bottle filled)	—	—
„ 15	9·2	3	3·6
„ 22	14·7	7	3·4
„ 26	10·2	4	3·4
July 11	16·7	45	2·8
„ 17	12·4	6	3·1
			Mean 3·3

At the conclusion of these experiments bottle (2) was washed out, dried and filled with 1620 gm. of coarsely powdered heat-dried gault. For the greater part this gault came from bottle (1) but more was added from the stock. Volume of bottle 1790 cc. Volume of air-spaces, by pressure 1330 cc., by water 1270 cc. The results obtained with this bottle are:

Date of testing	Emanation removed	Period of accumulation	Accumulation per day
July 28	(bottle filled)	—	—
Aug. 1	3·0	4	·96
„ 8	4·6	7	1·06
			Mean 1·0

The damp gault in bottle (1) when dried weighed 1400 gm. The daily growth of 3·2 for 1400 gm. of gault, when damp, corresponds to a radium-content of $\cdot 18 \times 10^{-12}$ gm. per gm. The daily growth of 1·0 for 1620 gm. of dry gault corresponds to a radium-content of $\cdot 05 \times 10^{-12}$ gm. radium per gm. of gault. Damp gault therefore gives off about three times as much emanation as dried gault.

Strutt found $1 \cdot 0 \times 10^{-12}$ gm. of radium per gm. of gault so that the supply of emanation to the air surrounding the gault is contributed to by only $\frac{1}{6}$th of the radium actually present in the gault when the gault is damp and by only $\frac{1}{20}$th when the gault is dry. It is worthy of note that strong indications of thorium-emanation were obtained with the gault.

(5) *Do the pipes and the bottles give consistent results?*

The results can only be taken as very approximate. The soil around the pipes is more compact than the soil in the bottles. I shall assume that the emanation in the air drawn up the pipe is in equilibrium with the radium in the soil.

Take the case of the 5-foot pipe at the Cavendish. The volume of the testing vessel alone is 3000 cc., so that 3000 cc. of air from this give a leak of from 20 on a wet day to 80 on a dry day, say 60 for a dryness corresponding to the undried soil in the bottle.

Now in the bottle we have 900 cc. of air in contact with about 2000 gm. soil and this gives a leak of 4·6 for a day's accumulation or 27 when in equilibrium. Then working from the bottle results we find that 3000 cc. of air from the soil should give a leak of $\frac{3000}{900} \times 27 = 90$ nearly, which is of the same order as that actually given.

Now take the case of the chalk. 3000 cc. of air from the pipe gives a leak of about 20 on the average.

The bottle contains 1450 cc. air associated with 3940 gm. (damp) chalk, and when in equilibrium the emanation in this air gives a leak of $7\frac{1}{2}$, whence 3000 cc. of air from the pipe should give a leak of

$$\frac{3000}{1450} \times 7\tfrac{1}{2} = 16 \text{ about,}$$

which is not far from 20.

(6) *The Variation of the results from the pipes during the* 6 *months* (March—August).

From the tables above it is evident that the Chalk pipe indicates no variation, the Observatory and Lawn pipes were very irregular, while the pipe in the court of the Cavendish certainly did give a fairly consistent temperature and rain variation. It is very curious why this pipe alone should show this effect.

For what reasons should one expect a variation? In wet weather the soil is full of water and one would expect the emanation in the particles of soil to be imprisoned by the shell of water, but as a set off against this it has been found that a soil when moist gives off more emanation than when dry. In very dry weather the upper layer of soil cracks and this might facilitate the supply of emanation to the pipe.

(7) *Comparison of the emanation-contents of ground-air and atmospheric-air.*

In a previous paper* it was shown that 630 litres of air passed through certain charcoal tubes yielded an amount of emanation represented on the scale used in these papers by 2·45. In another paper† it was shown that this was only about 62 °/₀ of the amount actually in the air, so that the mean actual amount may be represented by about 4·0, whence 3000 cc. (*i.e.* the volume of the testing vessel) would give an amount ·02. Compare this with the average amount of 50 given in average weather by the pipes in the gravel in Cambridge and we see that the ground-air is 2500 times as strong in radium-emanation as the atmospheric-air. From this we should expect that when the barometric pressure falls some of this emanation-charged air would escape from the ground and the emanation-content of the atmosphere would be increased. The author found just the reverse to occur, but this may be due to the fact that in England rain nearly always accompanies a barometric depression, and as we have seen above the Cavendish pipe yields less emanation in wet weather than in dry weather. In dry weather the large cracks formed in the ground may facilitate the supply of emanation to the air and thus partly account for the large emanation-content found in anticyclonic weather.

I wish to express my best thanks to Professor Sir J. J. Thomson for his helpful suggestions and kindly interest in these experiments.

Note added July 26th. In the current number of *Nature* there is an abstract of a paper read to the Royal Dublin Society by Prof. Joly and Mr Smyth describing experiments similar to the above. They find about the same quantity of emanation in the air of the soil around Dublin as I find near Cambridge.

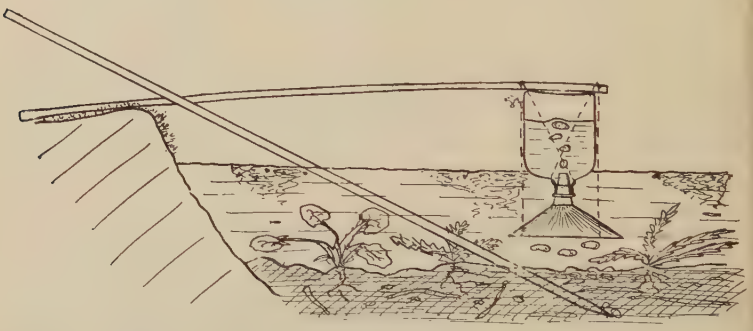
* *Phil. Mag.* VI, 20, July 1910. † *Ibid.* Oct. 1910.

The Radioactivity of Marsh Gas. By JOHN SATTERLY, D.Sc. (Lond.), M.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 21 August 1911.]

Marsh Gas is the name given to the gas which is liberated when the mud and decaying vegetable matter below slowly moving or stagnant water is disturbed. It consists largely of methane (CH_4). The gas is inflammable, and is supposed to be responsible for the phenomenon known as the Will-o'-the-Wisp or Jack-a-Lantern. The author has measured the amount of emanation in the air of the atmosphere*, in the air of the soil†, in the waters around Cambridge‡, and marsh gas being very plentiful in August due to the long spell of fine weather it was thought it would be interesting to sample it for radium emanation.

The neighbourhood of Cambridge is rich in stagnant back-waters and other ditches. At this time of the year the amount of marsh gas they yield is surprising. The supply varied in different places, but on the average between three and four litres of the gas could be collected in thirty minutes.



The collecting apparatus is shown in the diagram. It was simply a bottle attached by wire to a long batten. A short wide-angled funnel was provided to guide the liberated gas the way it should go. The bottle and funnel were first filled with water and then inverted. The mud at the bottom of the water was then vigorously poked with a pole and the gas collected as it rose. The funnel was detached and a stopper inserted into the neck of the bottle before the latter was removed from the water.

* *Phil. Mag.* Oct. 1908, July 1910.
† *Proc. Camb. Phil. Soc.* Vol. XVI.
‡ *Ibid.* Vols. XV. and XVI.

On returning to the laboratory the testing vessel (of volume 3 litres) was exhausted and filled with the gas*. The electrical leak was taken ten minutes after filling, as is usual in testing for radium emanation. To prove that the electrical activity of the gas was due to the presence of radium emanation the gas in one case was allowed to remain in the vessel for three hours and the leak taken again. It was found that the leak after the gas had been in the testing vessel three hours was fifty per cent. greater than the leak after the gas had only been in ten minutes. This is a sure test of radium emanation (with a testing vessel of the shape of mine)†. The growth of conductivity from the time of filling up to the ten-minute maximum and the decay of the active deposit in the vessel after the removal of the emanation also confirmed the presence of radium emanation in the gas. The marsh gas *in situ* may also contain thorium emanation, but in my method of testing this emanation would not be detected as it would have totally perished before I reached the laboratory.

The results obtained are given in the table on p. 358; the air-leak has been deducted from the observed leak and the result brought to a common sensitiveness, a 90 cm. deflection of my spot of light for a potential difference of one volt between the quadrants, before insertion into the last column. The normal air leak is usually about ·9 to 1·1 cm. per minute,

In all cases more gas was collected than was required to fill the testing vessel. The remainder was lighted, and it burnt with a pale blue flame for quite a time. In the cases of the samples from the Rifle Range and St John's the flame was more luminous than usual.

It will be observed from the results of Aug. 11th and 14th that there was more radium emanation in the marsh gas collected when the mud at the bottom of the water was more disturbed. This would be expected, for nearly all the emanation must come from the radium in the mud. The result from the pond at the Rifle Range is surprisingly low. It was for this reason that the second visit was paid, when an almost identical result was obtained. The great difference between this result and the others led me to test the waters of the Rifle Range pond and the Queens' back-water for radium emanation. Two litres of these waters were boiled and the emanation expelled by drawing air through the boiling water. The air was then passed into the testing vessel. The leaks obtained were ·01 and ·30 cm. per minute for the Rifle Range and the Queens' water respectively. This disparity is quite as great as that obtained for the marsh gas.

Previous standardisation experiments had shown that the amount

* The method of testing is described in my previous paper.

† *Phil. Mag.* July 1910.

Date 1911	Locality at which the gas was collected	Remarks on the nature of the water and its bed	Activity of the marsh gas expressed as leak in cms. per minute
Aug. 5	Backwater on Queens' Green, midway between Silver Street and King's	Fairly shallow and weedy, mud much disturbed during collection	85
,, 11	Backwater on Queens' Green towards the Silver Street end	Deep water, bottom fairly hard, cleaner weeds, gas came off readily	39
,, 12	Backwater alongside Erasmus' Walk	Very shallow, much duckweed, smelly, mud very slimy, much disturbed	74
,, 14	Same as Aug. 11th	Bottom disturbed more than on August 11th	48
,, 15	Hobson's Conduit, up the path field towards Trumpington	Only 3 inches of mud, then a hard bottom	50
,, 17 (1)	Pond behind the stop-butt at the University Rifle Range	Pool very shrunken, smelly, mud much disturbed	6
,, 17 (2)	Ditch to west of Coe Fen, North	Much duckweed above and black mud below. Plenty of gas	50
,, 18 (1)	Backwater, S.E. side of the Wilderness of St John's	Nearly dried up. Plenty of dark mud, very smelly, much gas	91
,, 18 (2)	On the Cam behind the Old Granary, near Silver Street Bridge	Bottom uneven, fairly hard in places, soft in others	83
,, 19	Same as Aug. 17th (1)	Same as Aug. 17th (1)	8
		Mean (excluding the Rifle Range results)	65

of emanation in equilibrium with $1{\cdot}57 \times 10^{-9}$ gm. of radium gives a leak of 120 cms. per minute when passed into the same testing vessel*, hence the amount of radium emanation in a litre of an average sample of marsh gas is equal to that which would be in equilibrium with $\frac{1}{3}$ of $\frac{65}{120}$ of $1{\cdot}57 \times 10^{-9}$ gm. of radium. This is equal to 3×10^{-10} gm. of radium, whence the radium content of marsh gas may be said to be 3×10^{-10} Curie.

This is approximately the same value as that for the air drawn up through pipes inserted to depths of from three to five feet in the soil in and about Cambridge town†.

It may be remarked that practically no rain had fallen in Cambridge for six or seven weeks when the above observations were made. The weather had been hot and dry with a fairly high barometer nearly all the time.

The author desires to return his best thanks to Mr H. Hickman for manipulating the stirring pole.

* *Proc. Camb. Phil. Soc.* Vol. xv, p. 543.

† *Ibid.* Vol. xvi, p. 355.

On the Radium-Content of Various Fresh and Sea Waters and some other Substances. By JOHN SATTERLY, D.Sc. (Lond.); M.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 29 August 1911.]

In the *Proceedings of the Cambridge Philosophical Society*, Vol. xv., Part vi. the author described some experiments made to measure the radium-content of Cambridge Tap Water and the water of the Cam. These have been repeated and further experiments of the same nature have been made on some other waters occurring in or near Cambridge, on some specimens of sea-water from around the coast and on a few other substances. The method of experiment and evaluation is exactly the same as that described in the above paper. In the majority of cases the amount of emanation which accumulated on standing was just within the range of measurement of the author's apparatus, so that the results can rarely be given beyond the first significant figure. In many cases a little powdered talc (about as much as will go on a sixpence) was added to the sample of water to produce free ebullition. This is recommended by Prof. Joly.

Fresh Water.

Table I gives the fresh-water results. The results for the dissolved emanation in the tap water and Cam water collected in February agree very well with the results given in the paper mentioned above, but the actual radium content of the water is distinctly less. This is no doubt due to the winter's rains. The water at Dale's Brewery is pumped up from a boring 250 feet deep which reaches down to the Lower Greensand. The Nine Wells water was collected at the springs just as the water flowed out from under the Chalk. The Laboratory distilled water gave a rather surprising result; one would have expected it to be quite free from radium. The sample taken, however, must have been rather exceptional, for other samples gave practically no accumulation and a solution of 200 gm. pure sulphate of sodium also gave none. The last three specimens quoted were collected towards the end of the long drought of 1911. The Cam water is distinctly poorer in dissolved emanation than in the specimen tested before.

Sea Water.

It was not intended to emulate Professors Joly and Eve in their work on the radium-content of sea water, but as they differ

TABLE I.

Specimen of Water and Treatment 1911	Observed leak less the air leak	Leak per litre of water	Accumulation per day per litre of water	Equivalent quantity of Radium in grams per litre of water
Cambridge Tap Water—				
(1) 2½ litres (+talc) Initial boiling, Feb. 8th	28·8	11·5	—	150×10^{-12}
(1) 2½ litres (+talc) Reboiled on Aug. 22nd...	too	small	to be	measured
(2) 2½ litres (+25 cc. HCl +talc) Initial boiling, Feb. 8th	25·8	10·3	—	135×10^{-12}
(2) 2½ litres (+25 cc. HCl +talc) Reboiled on Mar. 24th ...	·2	·06	·01	$·8 \times 10^{-12}$
(2) 2½ litres (+25 cc. HCl +talc) ,, ,, Aug. 22nd...	·1			
The Water of the Cam—				
(1) 2½ litres (+talc) Initial boiling, Feb. 14th	1·0	·4	—	5×10^{-12}
(1) 2½ litres (+talc) Reboiled on Mar. 24th ...	·05	·02	·003	$·3 \times 10^{-12}$
(1) 2½ litres (+talc) ,, ,, Aug. 22nd...	·05			
(2) 2½ litres (+25 cc. HCl +talc) Initial boiling, Feb. 14th	1·2	·5	—	7×10^{-12}
(2) 2½ litres (+25 cc. HCl +talc) Reboiled on Mar. 23rd ...	·15	·07	·01	$·9 \times 10^{-12}$
(2) 2½ litres (+25 cc. HCl +talc) ,, ,, Aug. 24th ...	·2			
Water from Dale's Brewery—				
2½ litres (+25 cc. HCl +talc) Initial boiling, Feb. 17th	37·8	15·1	—	196×10^{-12}
2½ litres (+25 cc. HCl +talc) Reboiled on Mar. 12th ...	·2	·07	·01	$·9 \times 10^{-12}$
2½ litres (+25 cc. HCl +talc) ,, ,, Aug. 23rd ...	·14			
Water from Nine Wells—				
2 litres (+20 cc. HCl +talc) Initial boiling, Feb. 23rd	20·0	10·0	—	130×10^{-12}
2 litres (+20 cc. HCl +talc) Reboiled on Aug. 23rd ...	too	small	to be	measured
The Laboratory Distilled Water—				
2 litres (talc added Dec. 7th) Initial boiling, Nov. 24th	not	measured		
2 litres (talc added Dec. 7th) Reboiled on Dec. 6th.....	·07			
2 litres (talc added Dec. 7th) ,, ,, Mar. 17th ...	·15	·04	·007	$·5 \times 10^{-12}$
2 litres (talc added Dec. 7th) ,, ,, Aug. 23rd ...	·03			
Queens' Green Backwater—				
1¾ lit. +4 cc. HCl, Initial boiling, Aug. 18th	·3	·17	—	2×10^{-12}
Pond on Rifle Range—				
1¾ lit. +4 cc. HCl, Initial boiling, Aug. 19th	·01	·005	—	$·07 \times 10^{-12}$
The Water of the Cam—				
1¾ lit. +4 cc. HCl, Initial boiling, Aug. 19th	·2	·1	—	1×10^{-12}

somewhat in their results, Professor Joly* giving a mean radium-content of 16×10^{-12} gm. of radium per litre of sea-water and Professor Eve† $\cdot 9 \times 10^{-12}$, it was thought it would be interesting while the necessary apparatus was set up to analyse a few specimens of sea-water from around our coasts. By the kindness of correspondents at Hunstanton, Dover and Weymouth, samples were obtained from the deep water at high tide off the pier heads at these places. The results are given in Table II.

TABLE II.

Specimen of Water and Treatment	Observed leak less the air leak	Observed leak less the air leak per litre of water	Accumulation per day per litre of water	Radium content in grams per litre of water
Hunstanton—				
Initial boiling, Dec. 9th	·15	—	—	—
Reboiled on Dec. 19th...	·6			
$3\frac{1}{4}$ litres, 20 cc. HCl added Feb. 8th: „ „ Jan. 13th...	·2			
„ „ Feb. 7th ...	·3 (·36)	·1	·02	$1{\cdot}6 \times 10^{-12}$
„ „ Mar. 22nd...	·4			
„ „ Aug. 24th...	·3			
Dover—				
$3\frac{1}{2}$ litres: Initial boiling, Jan. 13th	not measured			
Reboiled on Feb. 22nd...	·07	·02	·003	$\cdot 3 \times 10^{-12}$
$2\frac{1}{2}$ litres taken + 20 cc. HCl: „ „ Aug. 24th...	·1	·04	·007	$\cdot 5 \times 10^{-12}$
Weymouth—				
(1) 2 litres + 50 cc. HCl: Initial boiling, Jan. 16th	·3	—	—	—
Reboiled on Feb. 23rd...	·17	·08	·014	$1{\cdot}2 \times 10^{-12}$
„ „ Mar. 23rd...	·05	·02	·004	$\cdot 3 \times 10^{-12}$
(2) $2\frac{1}{4}$ litres, no HCl: Initial boiling, Jan. 17th	·3	—	—	—
Reboiled on Feb. 23rd ...	·16	·08	·012	$1{\cdot}0 \times 10^{-12}$
„ „ Mar. 22nd...	·02	·01	·002	$\cdot 2 \times 10^{-12}$
(1) and (2) ..... Reboiled separately on Aug. 24th, but the collected air added together	·07	·02	·003	$\cdot 3 \times 10^{-12}$

* *Phil. Mag.* Sept. 1909. † *Ibid.* July 1909.

The result of adding hydrochloric acid to the water seems to end up the amount of emanation liberated. This is evidently due to the solution power of the acid on the various salts in the water. The results obtained with the Weymouth water on March 22nd and 23rd are very low compared to the results of February 23rd. The reason for this is not apparent. The result of August 24th is in agreement with the low results. On the whole the results above agree with Eve's results rather than with Joly's, but too much stress must not be laid on the results on such a small number of analyses.

TABLE III.

Specimen and Treatment		Observed leak less the air leak	Accumulation per day	Equivalent quantity of Radium in grams
Mixture of 15 gm. talc, 50 cc. HCl and 1 litre distilled water	Initial boiling, Feb. 14th	·55	—	—
	Reboiled on Mar. 17th ...	·3	·06	$4·8 \times 10^{-12}$
	,, ,, Aug. 24th ...	·4		
Strong hydrochloric acid, pure (½ litre)	Initial boiling, Dec. 20th	—	—	—
	Reboiled on Jan. 12th ...	too	small	to be measured
Boiler Fur Solution	Made on Dec. 23rd	—	—	—
	Reboiled on Jan. 13th ...	·4	·08	$2·4 \times 10^{-14}$ per gm. of "fur" *
	,, ,, Feb. 17th ...	·6		
	,, ,, Aug. 25th ...	·4		
Sugar Solution ...	Made on Jan. 14th	—	—	—
	Reboiled on Jan. 26th ...	·1	·1	$·02 \times 10^{-12}$ per gm. of sugar *
	,, ,, Feb. 25th ...	·1		
	,, ,, Aug. 24th ...	·1		
Thorium Solution	Made in March, 1906 ...	—	—	—
	Reboiled, Jan. 20th, 1911	—	—	—
	,, after a 70 hrs' rest	13·8	5·6	$7·7 \times 10^{-11}$ per gm. of thorium hydroxide *
	,, after a 48 hrs' rest	10·5	5·8	5·7

* In calculating these results I have assumed that the acid and distilled water used was free from radium.

Various Substances.

The talc and hydrochloric acid used in the above experiments were tested; the results are given in Table III together with results obtained from solutions of boiler fur in hydrochloric acid, sugar in water and thorium hydroxide in nitric acid. The first solution was made by dissolving 273 gms. of boiler fur (obtained in a kitchen range from Cambridge water) in 600 cc. strong hydrochloric acid and adding 250 cc. distilled water. The sugar solution contained 438 gms. of ordinary loaf sugar dissolved in about 1 litre of distilled water. The thorium solution was made in 1906 by dissolving 5·8 gms. of thorium hydroxide in nitric acid and making up to 200 cc. with distilled water. The thorium hydroxide was obtained from the firm of Armet de Lisle of Paris, and the guarantee with it stated that it contained $9{\cdot}7 \times 10^{-6}$ gms. of radium per gram of oxide of thorium. My test in 1911 shewed a much smaller amount. Another sample of thorium hydroxide obtained from the same firm in 1906 and under the same guarantee was found this year to contain $1{\cdot}6 \times 10^{-10}$ gms. of radium per gram of hydroxide.

Summary.

(i) Various fresh waters from the neighbourhood of Cambridge have been analysed for radium. They all shew a high amount of dissolved emanation, much more than can be accounted for by the quantity of radium actually in solution in the water. The spring waters show much more dissolved emanation than the water of the Cam, although the actual radium-content is about the same.

(ii) Three specimens of sea water have been analysed for radium. The mean radium-content is about $1{\cdot}0 \times 10^{-12}$ gm. of radium per litre of sea water. This agrees very nearly with Professor Eve's results and is much lower than those of Professor Joly's.

On the Scattered Röntgen Radiation from different Radiators.

By J. A. Crowther, M.A., St John's College.

[*Read* 22 May 1911.]

It has been generally assumed that the amount of scattered Röntgen radiation from a given mass of a radiator is independent of the chemical nature of the radiator. The assumption rests mainly on experiments made on elements of low atomic weight*, for which the characteristic secondary radiation is either not excited or is too small to be appreciable. For elements of higher atomic weight than sulphur, the scattered radiation is masked by large amounts of true secondary radiation, and, so far as I am aware, no experiments have been made to determine the actual proportion of the primary Röntgen radiation scattered by these heavier elements.

In the course of some measurements on the distribution of the secondary Röntgen radiation, an attempt was made to separate the two effects for one or two of the heavier metals, and it was found that the results obtained for the scattered radiation were larger than should have been expected if the scattering were simply proportional to the mass of the radiator. The apparatus was not designed to give the actual proportion of the primary beam scattered, as there was some uncertainty as to the amount of absorption of the secondary beam in the radiator. It was decided to repeat the experiments with a modified form of the apparatus.

The apparatus used is shewn in plan in Fig. 1. The ionization chamber S used to measure the secondary rays is the one previously described. It was mounted on a carriage which could move on a circular geometrical slide about a centre O. P was a small ionization chamber, just large enough to include the whole cross section of the primary beam. The primary beam was limited by the stops A, A to a narrow pencil of rectangular cross section. The lead screens L, L served to shield the ionization chambers from stray radiations. The ionization chambers were connected to two electroscopes, mounted on a rigid stand above the rest of the apparatus, in the same way as in the previous experiments. The radiator R was mounted on an aluminium frame, and could rotate on a vertical axis through O, the centre of the slide. It could thus be inclined at any desired angle with the primary beam. In making the measurements the radiator was set so that its normal bisected the angle between the direction of the primary beam and the position of the chamber S. In this way it is easy to

* J. A. Crowther, *Phil. Mag.* S. vi, Vol. xiv. p. 653.

shew that the absorption of the primary and of the scattered radiation in the radiator is at any rate very approximately the same. It is thus not necessary to know the exact absorbability of the rays used in the material of the radiator.

Experiments have been made on paper, aluminium, copper, nickel, and tin. The two first are not known to emit any homogeneous radiations; the radiations from nickel and copper are very soft and could be easily absorbed by a cm. or so of aluminium board. The characteristic radiation from tin is very hard and is not excited by a soft bulb. The intermediate elements are more difficult to work with and have not yet been investigated.

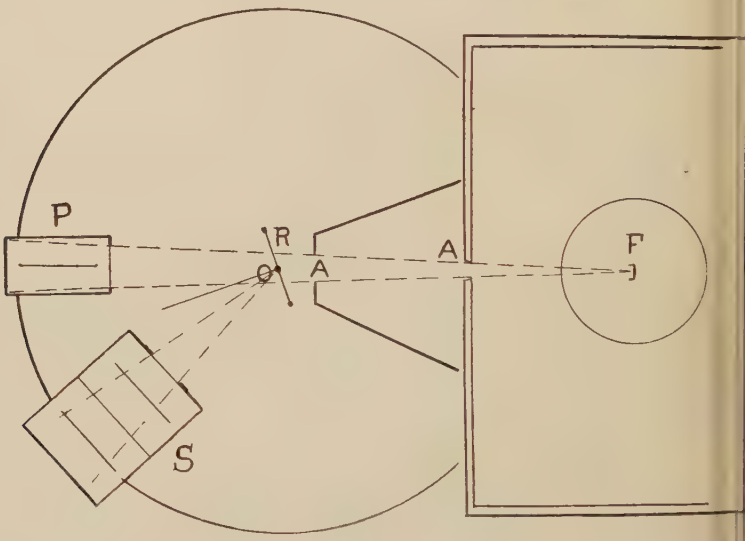


Fig. 1.

In every case sufficient positions of the secondary chamber were taken to enable the distribution curve of the scattered radiation to be determined. In every case the distribution characteristic of the scattered radiation was found.

The results obtained are given in Table I. The first column gives the material of the radiator; the second the ratio of the intensities of the secondary radiation at angles of 30° with the primary beam, in the forward and backward directions, and serves as a measure of the eccentricity of the distribution curve. The last column gives the whole intensity of the scattered Röntgen radiation, as deduced from the intensity at an angle of 90° with the primary beam and the distribution curve*. The figures are

* See J. A. Crowther, *Proc. Roy. Soc.* A, Vol. LXXXV. p. 41.

n arbitrary units and are for radiators having equal masses per nit area. The mass of radiator traversed by the primary beam is ius the same in all cases.

TABLE I.

Radiator	$I_{+30°}/I_{-30°}$	Scattering per unit mass
Paper	1·3	·40
Aluminium...	2·8	·42
Nickel.....	1·6	1·4
Copper	1·7	1·4
Tin	1·7	2·2

Taking this last column, it will be seen that the intensity of e radiation scattered from equal masses of different materials is ot independent of the nature of the radiator. It increases very ppreciably as the atomic weight of the radiator is increased. hus the scattered radiation from tin is at least four times that om filter paper. Some years ago I shewed* that the scattered diation from hydrogen was mass for mass considerably greater an the scattered radiation from air, and higher values were also btained with helium and sulphur dioxide. Assuming that the stribution of the scattered radiation is the same for these gases for filter paper, we can include these elements provisionally in r Table, and taking carbon or oxygen as unity we get the values ven in Table II. It will be seen that the scattered radiation is minimum for elements in the neighbourhood of carbon and ygen, and increases both for elements of smaller and higher omic weights.

Consider now the second column of Table I. The figures give e ratio of the intensities in a forward and backward direction, d measure the eccentricity of the distribution. It will be seen at the eccentricity is not the same for all substances. For paper is comparatively small; for aluminium it is very considerable, minium shewing by far the largest effect. The values for the her elements tried are intermediate between these values, and ry nearly equal.

Experiments made with different thicknesses of aluminium ve shewn that for this element the eccentricity depends on the ickness of the radiator employed. The results for aluminium

* *Phil. Mag.* S. vi, Vol. xiv. p. 654.

TABLE II.

Element	Atomic weight	Relative scattering by equal masses
Hydrogen ...	1	1·7
Helium	4	1·1
Carbon	12	1·0
Nitrogen.....	14	1·0
Oxygen	16	1·0
Aluminium...	27	1·1
Sulphur	32	1·4
Nickel.....	59	3·5
Copper	63·5	3·5
Tin	118	5·5

TABLE III.

Thickness mm.	$I_{+30^\circ}/I_{-30^\circ}$	$I_{\pi/2}/P$	$I_{\pi/2}/P.d$
·24	3·2	·19	·79
·61	2·8	·49	·80
1·11	2·7	·86	·78
2·04	2·3	1·59	·78
3·15	2·2	2·43	·77
5·04	1·6	3·91	·78

adiators of different thicknesses are given in the second column f Table III. It will be seen that the ratio of the intensities of he scattered Röntgen radiation at 30° with the primary beam, in he forward and backward directions respectively, decreases from ·3 for a very thin radiator to 1·6 for a fairly thick one. The latter alue is very near that found for tin and copper. It is probably nly a coincidence, but it may be worth while pointing out that he ratio of the intensities decreases almost exactly exponentially ith the thickness of the radiator.

At the same time too much importance should not be attached o this variation. Owen has shewn that the eccentricity of the istribution of the scattered radiation is very much less for hard nan for soft rays, and it is possible that the results obtained are ue, at least in part, to the gradual filtering out of the softer onstituents from the rather mixed pencil of primary rays emitted y the focus tube, as more and more aluminium is placed in the ath of the rays.

Measurements were also made of the intensity of the scattered idiation at an angle of 90° with the primary beam. The ratio of he scattered radiation in this direction to that of the primary beam s measured by the chamber P is given in the third column of able III. This ratio divided by the corresponding mass per unit rea of the radiator is given in the last column of the same Table. t will be seen that within the limits of experimental error the tio is a constant. The intensity of the scattered radiation in his direction is thus directly proportional to the thickness of the diator.

The fact that the amount of Röntgen radiation scattered per nit mass of radiator was supposed to be independent of its nemical nature has been used as evidence that the number of ectrons in the atom is simply proportional to the atomic weight. he fact that this independence is not found to hold good does ot necessarily disprove this assumption. It is possible that the ectrons when very closely packed together may influence each her's vibrations. In an earlier paper* I have shewn that the mount of radiation scattered by a given atom is independent f its state of chemical combination, but it is quite possible that e very much closer aggregation of electrons in the atom itself ay have an appreciable effect. This point is one of some nportance and is still under investigation.

* *Loc. cit.*

The Multiplication of Fourier Series. By Professor A. C. Dixon, Sc.D., F.R.S.

[*Received* 27 July 1911.]

If $f(x)$, $g(x)$ are two functions bounded and summable in an interval I enclosing a, b, $a+x$, $b+x$, then

$$F(x) = \int_a^b f(t)\, g(t+x)\, dt$$

is a continuous function of x. For

$$\left| F(x_1) - F(x) \right| = \left| \int_a^b f(t) \{ g(t+x_1) - g(t+x) \}\, dt \right|$$
$$< k \int_a^b \left| g(t+x_1) - g(t+x) \right| dx,$$

if $|f(t)|$ always $< k$; and this tends to zero with $x_1 - x$ if $a+x_1$, $b+x_1$, $a+x$, $b+x$ are all within the interval I. (Lebesgue, *Séries trigonométriques*, pp. 15, 16.)

The argument still applies when f is bounded and $|g|$ summable and the result may be further extended as follows.

To assign a value to $\int_a^b \phi(t)\, dt$ when ϕ is not bounded, we may follow Harnack, enclosing the set of points of infinite discontinuity of ϕ, supposed to be of zero measure, in a system of intervals e_n, and taking a function ϕ_n vanishing at the points of e_n and equal to ϕ elsewhere. Then ϕ_n is bounded, and if $\int_a^b \phi_n(t)\, dt$ (in Lebesgue's sense) tends to a limit when the content of e_n tends to zero, and if that limit is independent of the method of formation of e_n, then that limit is taken to be the value of $\int_a^b \phi(t)\, dt$.

In the present case $\phi(t) = f(t)\, g(t+x)$, whose infinite discontinuities are among those of $f(t)$ and $g(t+x)$. Thus a special method of forming ϕ_n is to form f_n and g_n on the same principle and take their product. Since f_n, g_n are bounded the function

$$F_n(x) = \int_a^b f_n(t)\, g_n(t+x)\, dt$$

is continuous.

Now

$$F(x_1) - F(x) = \{ F(x_1) - F_n(x_1) \}$$
$$+ \{ F_n(x_1) - F_n(x) \} - \{ F(x) - F_n(x) \},$$

and therefore if in any interval of x, $F_n(x)$ tends uniformly to $F(x)$ when e_n is diminished, $F(x)$ is a continuous function of x.

It is not necessary for this that the limit $F(x)$ should be independent of the method of formation of e_n, and thus the integral need not exist: $F(x)$ may be called a special value of the integral.

Hence, *if the infinite discontinuities of* $f(x)$, $g(x)$ *can be inclosed in a set of intervals* e_n, *of arbitrarily small content, and if* $F_n(x)$ *denotes*

$$\int_a^b f_n(t)\, g_n(t+x)\, dt,$$

where $f_n(x) = g_n(x) = 0$ *within* e_n *and* $f_n = f$, $g_n = g$ *elsewhere: if also when the content of* $e_n \to 0$ *according to a certain method* $F_n(x) \to F(x)$ *uniformly within an interval* (α, β) *of* x, *then* $F(x)$ *is a continuous function of* x *within* (α, β).

In particular if $\int_a^b f(t)\, g(t+x)\, dt$ is uniformly and absolutely convergent within (α, β) it is a continuous function of x within (α, β).

Further, if $F(x)$ has a Fourier series, the sum of that series is found by Césaro's method of arithmetic means, say for convenience the "mean sum," is equal to $F(x)$ since $F(x)$ is continuous. Suppose then that f, g have the period 2π and that $a = 0$, $b = 2\pi$; let A_p, B_p be the coefficients of $\cos px$, $\sin px$ in the Fourier series of $F(x)$, and $\frac{1}{2}A_0$ the constant term.

$$\pi A_p = \int_0^{2\pi} F(x) \cos px\, dx.$$

$$\int_0^{2\pi} F_n(x) \cos px\, dx = \int_0^{2\pi}\int_0^{2\pi} f_n(t)\, g_n(t+x) \cos px\, dt\, dx$$

$$= \int_0^{2\pi}\int_0^{2\pi} f_n(t)\, g_n(t+x) \cos px\, dx\, dt,$$

since the subject is bounded,

$$= \int_0^{2\pi}\int_t^{2\pi+t} f_n(t)\, g_n(u) \cos p(u-t)\, du\, dt$$

$$= \pi^2 (a_{n,p} a'_{n,p} + b_{n,p} b'_{n,p}),$$

where $a_{n,p}$, $b_{n,p}$ are Fourier coefficients of f_n, and $a'_{n,p}$, $b'_{n,p}$ Fourier coefficients of g_n.

Thus $$A_p = \pi (a_p a_p' + b_p b_p'),$$

if (1) $$\int_0^{2\pi} F(x) \cos px\, dx = \lim \int_0^{2\pi} F_n(x) \cos px\, dx,$$

and (2) $a_{n,p}$, $b_{n,p}$, $a'_{n,p}$, $b'_{n,p}$ tend to limits a_p, b_p, a_p', b_p'.

Under like restrictions by the same method

$$B_p = \pi (a_p b_p' - a_p' b_p), \qquad A_0 = \pi a_0 a_0'.$$

One of the restrictions (2) is that $a_{n,p}$ must tend to a limit,

that is, $a_{m,p} - a_{n,p}$ must $\to 0$ when m, n are both increased indefinitely in any way. Now

$$a_{m,p} - a_{n,p} = \int_0^{2\pi} \{f_m(t) - f_n(t)\} \cos pt\, dt,$$

and this range of integration may be broken up into $4p$ parts $(0, \pi/2p)(\pi/2p, \pi/p) \ldots$ in each of which $\cos pt$ is of constant sign and monotone. Hence by the second mean-value theorem each of the $4p$ parts may be put equal to $\int_\alpha^\beta (f_m - f_n)\, dt$ for some values of α, β belonging to the part. Hence, if over every partial interval $\left| \int (f_m - f_n)\, dt \right| < \epsilon$, where ϵ is the same for all intervals and $\to 0$ when m, n are increased, the limit a_p exists for any finite value of p; similarly for b_p, a_p' b_p'.

The restriction (1) is similarly satisfied if over every partial interval

$$\left| \int (F - F_n)\, dt \right| < \epsilon,$$

where ϵ is the same for all intervals and $\to 0$ when n is increased, and we have further implied the existence of the limit F for all values of x except at most a set of measure zero.

There is no real loss of generality through putting $x = 0$, since by applying the theorem so modified to $f(t)$ and $g(t + a)$, we can deduce it for any other value of x. *Hence the following result: the mean sum of the series*

$$\tfrac{1}{2} a_0 a_0' + \sum_1^\infty (a_p a_p' + b_p b_p') \text{ is equal to } \frac{1}{\pi} \int_0^{2\pi} f(x)\, g(x)\, dx,$$

where the integrals involved, including the Fourier constants a_0, $b_0 \ldots$, have their special values and the functions satisfy the following conditions:

(*a*) $\left| \int (f_m - f_n)\, dx \right| < \epsilon$ over any interval, where ϵ is the same for all intervals not exceeding 2π and tends to zero when m, n are both increased indefinitely in any way.

(*b*) the same is true for $\left| \int (g_m - g_n)\, dx \right|$.

(*c*) $F_n(x)$ or $\int_0^{2\pi} f_n(t)\, g_n(t + x)\, dt$ tends to a limit $F(x)$ for all values of x except possibly a set of zero measure.

(*d*) $F_n(x)$ tends uniformly to $F(x)$ in an interval including the origin.

(*e*) $\left| \int (F - F_n)\, dt \right| < \epsilon$ over any interval, where ϵ is the same

for all intervals not exceeding 2π and tends to zero when n is increased indefinitely.

Of these (a), (b) are necessary for the existence of the Fourier constants of f, g in the special sense, (d) secures the continuity of $F(x)$ at the origin and may be replaced by any other condition securing the continuity at the origin of the limit of the sequence of continuous functions F_n: some condition of this nature appears to be indispensable, but it would be enough if it secured the continuity of $F(x)+F(-x)$, the limit of the sequence

$$F_n(x)+F_n(-x),$$

when $x=0$. The conditions (c), (e) do not at first sight seem so necessary.

When the integrals of f, g over the whole period 2π converge absolutely, say to A, B, the conditions (a), (b) are satisfied and so are (c), (e), as will now be proved. All cases may as usual be reduced to that in which f, g are always positive.

The auxiliary functions f_n, g_n will now be taken so that $f_n = L_n$ when $f > L_n$ and $g_n = L_n$ when $g > L_n$ and $L_n \to \infty$ with n.

Since $f(x)$, $g(x)$, $f_n(x)$, $g_n(x)$ are separately measurable* in x, it follows that $f(x)\,g(x+y)$ and $f_n(x)\,g_n(x+y)$ are measurable in the plane as well as in x only. Let Q denote the square, each of whose sides is 2π. Then since f_n, g_n are limited we have

$$\int_0^{2\pi}\int_0^{2\pi} f_n(t)\,g_n(t+x)\,dt\,dx = \iint_Q f_n(t)\,g_n(t+x)\,(dt\,dx)$$
$$= \int_0^{2\pi}\int_0^{2\pi} f_n(t)\,g_n(t+x)\,dx\,dt$$
$$= AB-\epsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

where ϵ now means "an arbitrarily small quantity."

Thus a limited function, namely $f_n(t)\,g_n(t+x)$, exists which nowhere exceeds $f(t)\,g(t+x)$ and whose double and both repeated integrals over Q are arbitrarily near to AB.

To prove the convergence of the double integral let $\phi(x,t)$ be any bounded function in Q which is always positive but nowhere exceeds $f(t)\,g(t+x)$. Let K be the upper limit of $\phi(x,t)$.

Then $\phi(x,t)+f_n(t)+g_n(t+x)+1$ has $K+2L_n+1$ for its upper limit and it nowhere exceeds $\{1+f(t)\}\{1+g(t+x)\}$. This expression has the advantage for our purpose that its factors have a lower boundary at least equal to 1.

Now take m so that $L_m \geqslant K+2L_n$, and it is impossible for

$$\phi(x,t)+f_n(t)+g_n(t+x)+1$$

to exceed $\qquad \{1+f_m(t)\}\{1+g_m(t+x)\}$.

* As in the later writings of Lebesgue and others, 'measurable' differs from 'summable' in not implying the convergence of the integral.

If this were possible we should have

$$\{1+f(t)\}\{1+g(t+x)\} > \{1+f_m(t)\}\{1+g_m(t+x)\},$$

and therefore $$1+f(t) > 1+f_m(t),$$

or else $$1+g(t+x) > 1+g_m(t+x),$$

or both. If we suppose $1+f > 1+f_m$, we have $f_m = L_m$, and therefore

$$\begin{aligned}(1+f_m)(1+g_m) &\geqslant (1+L_m)\times 1\\ &\geqslant 1+2L_n+K\\ &\geqslant 1+f_n(t)+g_n(t+x)+\phi(x,t),\end{aligned}$$

which is contrary to supposition. Similarly if $1+g > 1+g_m$. Hence

$$\begin{aligned}\phi(x,t)+f_n(t)+g_n(t+x)+1\\ \leqslant f_m(t)\,g_m(t+x)+f_m(t)+g_m(t+x)+1,\end{aligned}$$

and*

$$\begin{aligned}\operatorname*{sup}\iint_Q \phi(x,t)\,(dtdx) &\leqslant \iint_Q f_m(t)\,g_m(t+x)\,(dtdx)\\ &\quad+\iint_Q \{f_m(t)-f_n(t)\}\,(dtdx)\\ &\quad+\iint_Q \{g_m(t+x)-g_n(t+x)\}\,(dtdx)\\ &\leqslant AB+\epsilon\\ &\leqslant AB.\end{aligned}$$

Since $\phi(x,t)$ is any bounded function which nowhere exceeds $f(t)\,g(t+x)$ this result shews that the double integral of $f(t)\,g(t+x)$ over Q is convergent, and therefore by (1) equal to AB.

As to the second repeated integral $\int_0^{2\pi} F(x)\,dx$, let $\Phi(x)$ be any limited positive function of x which nowhere exceeds $F(x)$. Then by the nature of the improper integral $F(x)$ we have, if α is any positive quantity,

$$\Phi(x)-\alpha \leqslant \int_0^{2\pi} G(t,x)\,dt,$$

where $G(t,x)$ is limited and positive and nowhere exceeds $f(t)\,g(t+x)$.

We do not need to assume that G is summable in the plane, for if G_1 is limited and summable in the plane and everywhere $\geqslant G$, we have

$$\operatorname*{sup}_0^{2\pi}\operatorname*{sup}_0^{2\pi} G_1(t,x)\,dtdx \leqslant \iint_Q G_1(t,x)\,(dtdx)$$

* The suffix "sup" indicates the upper Lebesgue integral.

(Hobson, *F. R. V.* p. 580; Lebesgue, *Annali di Mat.* ser. 3, vol. VII, p. 279).

Thus,

$$\int_{\sup}^{2\pi}\int_{\sup}^{2\pi} G(t,x)\,dt\,dx \leqslant \iint_{\sup,Q} G(t,x)\,(dt\,dx) + \epsilon$$

$$\leqslant \iint_{\sup,Q} G(t,x)\,(dt\,dx),$$

and since $$\int_{\sup}^{2\pi} \Phi(x)\,dx - 2\pi\alpha \leqslant \int_{\sup}^{2\pi}\int_{0}^{2\pi} G(t,x)\,dt\,dx,$$

where α may be made small, while

$$\iint_{\sup,Q} G(t,x)\,(dt\,dx) \leqslant \iint_{Q} f(t)\,g(t+x)\,(dt\,dx) \text{ or } AB,$$

we have $$\int_{\sup}^{2\pi} \Phi(x)\,dx \leqslant AB,$$

so that $\int_0^{2\pi} F(x)\,dx$ converges and by (1) has the value AB. It follows that the values of x for which $F(x)$ itself diverges form a set of measure zero, and thus the conditions (c), (e) are both satisfied.

Hence, *if* $\int_0^{2\pi} f(x)\,dx$ *and* $\int_0^{2\pi} g(x)\,dx$ *are absolutely convergent the mean sum of the series* $\frac{1}{2}a_0a_0' + \sum_1^\infty (a_pa_p' + b_pb_p')$ *is equal to* $\frac{1}{\pi}\int_0^{2\pi} f(x)\,g(x)\,dx$, *provided that* $F_n(x)$ *tends uniformly to* $F(x)$ *in an interval including the origin:* it follows that *the mean sum of the series* $\frac{1}{2}a_0a_0' + \sum_1^\infty \{(a_pa_p' + b_pb_p')\cos px + (a_pb_p' - a_p'b_p)\sin px\}$ *is equal to* $\frac{1}{\pi}\int_0^{2\pi} f(t)\,g(t+x)\,dt$, *provided that* $F_n(x)$ *tends uniformly to* $F(x)$ *in an interval including* x, and for the condition of uniform convergency there may be substituted any less stringent condition which secures the continuity at x of the limit F of the sequence of continuous functions F_n.

[Several important papers by W. H. Young on this subject have lately appeared in the *Proceedings* of the R. S. and L. M. S. The present is a sequel to one by the writer in these *Proceedings*, vol. 15, pp. 210—216.]

The Photo-Electric Effects of Certain Compounds. By A. Ll. Hughes, M.Sc., B.A., Research Scholar of Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 18 August 1911.]

Our knowledge of the ionization by ultra-violet light is mainly derived from experiments on the emission of negative electricity from metallic surfaces exposed to the light. The number of experiments recorded on the ionization of gases by ultra-violet light is small in comparison. The only experiments that have been made on the nature of ionization by ultra-violet light are those on the mobility of the ions produced. At present, the conditions to be fulfilled before ionization of gases by ultra-violet light can be obtained are such that it is very difficult to make any experiments on the mechanism of the ionization by light. Thus light of wave length less than about $\lambda 1350$ is required before any appreciable ionization is obtained in air, and the fluorite of the necessary transparency is rare and expensive. Moreover, special arrangements have to be made to avoid a photo-electric effect (which may be big enough to mask the ionization in the air) due to scattered or reflected light at the surfaces of the electrodes. A few vapours, such as mercury* and anthracene†, can be ionized by the ultra-violet light from a mercury arc, but experiments on such vapours are difficult because the whole apparatus has to be maintained at a high temperature.

That our knowledge of the nature of ionization by α, β, γ and X-rays is much more definite than that of the nature of ionization by ultra-violet light, is largely due to the fact that experimenters have found it most convenient to study the ionization by α, β, γ and X-rays in a gas or vapour. The interpretation of ionization experiments on gases is greatly facilitated by the comparative simplicity of our conception of a gas. When we study ionization by ultra-violet light at a solid surface, we are not only handicapped by the want of a simple theory of the molecular state of a solid, but, in addition, our experiments are liable to much greater uncertainty. The absorption coefficient of these photo-electrons is so large that those which emerge from a metal surface can only come from an exceedingly thin layer, probably not many molecules in thickness. Conclusions involving the nature and properties of the solid become doubtful when we consider that the effective surface layer is probably appreciably different from the rest of the solid. Films of condensed gas, oxide, etc., can only be avoided by

* Steubing, *Phys. Zeit.* 1909, x. 787.
† Stark, *ibid.* x. 614.

special precautions, and, even then, it cannot be said with confidence that the effective surface layer is the same as the interior. Such considerations illustrate the uncertainties attending the interpretation of experiments on solids, and indicate how they may be avoided by investigations on gases instead of on solids. The problem, therefore, was to find some gas or vapour which could be ionized at ordinary temperatures by light of moderately long wave length such as the mercury arc emits. It appeared most likely that the desired result would be obtained with vapours containing elements which are known to be photo-electric.

The vapours tried were carbon bisulphide, carbon dioxide, tin tetrachloride, and zinc ethyl. In no case was there any trace of ionization observed, using the light from a mercury arc (shortest wave length about λ2300).

Carbon bisulphide.

The ionization chamber was a zinc cylinder of $4\frac{1}{2}$ litres capacity and arranged as in fig. 1. The inner electrode was made of linen gauze, the threads being about 3 mms. apart. The gauze was covered with soap solution to diminish the surface effect. The photo-electric effect at the zinc surface was avoided by always working with the ionization chamber at a positive potential. The light from a quartz mercury lamp (10 cms. away) passed into the chamber through a quartz window 3·8 cms. in diameter. When the apparatus was filled with air, there was a small leak due to the photo-electric effect at the inner electrode, which shows that the soap solution is photo-electric to a certain extent. The leak increased slightly with the potential, a variation which is characteristic of surface effects in the presence of a gas. This is shown in the following table.

Potential of case	Leak
+ 400 volts	$35{\cdot}2 \times 10^{-13}$ amp.
+ 200 „	31·2 „ „
+ 80 „	23·0 „ „

On drawing air into the apparatus through CS_2 and a plug of cotton wool to keep out nuclei, it was found that the leak had disappeared. After allowing for the natural leak, the leak due to the light, if any existed at all, was certainly less than $\cdot 2 \times 10^{-13}$ amp.,

the case being kept at + 400 volts. This shows that not only was there no ionization in the CS_2 due to the light, but also that the CS_2 absorbed the light, which caused the inner electrode to emit negative electricity. This might be expected from the spectroscopic result that CS_2 vapour has an absorption band from $\lambda 3300$ to $\lambda 2980$*. Incidentally, it shows that soap-solution is not photo-electric to light of wave length greater than $\lambda 3300$. The sodium in the soap solution is, of course, photo-electric with visible light.

Let us now calculate the order of the leak to be expected in the CS_2 on the assumption that chemical combination does not affect the photo-electric properties of carbon. A current of the order of 10^{-10} amp. per sq. cm. has been obtained from a carbon surface placed at a distance of about 10 cms. from the arc. Now the aperture of the quartz window is $\pi (1{\cdot}9)^2$ sq. cms. or 11 sq. cms. On the above assumption we should expect a leak of 11×10^{-10} amp., or say 10^{-9} amp. But experiment shows that the leak was certainly less than $\cdot 2 \times 10^{-13}$ amp. or about 10^5 times less than that calculated as above. If we consider that the number of electrons which emerge from a carbon surface is probably only a fraction of the total number produced there, then this number 10^5 is an underestimate.

Some earlier experiments which I carried out on CO_2 showed that it was as difficult to ionize as air. The wave lengths used in the experiments referred to were considerably shorter ($\doteq \lambda 1500$) than those employed in the present experiments.

Zinc ethyl.

The apparatus used for this experiment is shown in fig. 1. The volume is 500 c.c. On account of the chemical properties of zinc ethyl, quartz insulation was used instead of ebonite and the inner electrode (a ring crossed by a few fine wires) was covered with soot instead of soap solution as in the previous experiment. On the right is a simple apparatus B for measuring the leak from a zinc plate in vacuo. The ionization chamber had two quartz windows so that the absorption of $Zn(C_2H_5)_2$ for light causing a photo-electric effect at the zinc plate could be observed.

When the ionization chamber was evacuated, the photo-electric current from the zinc plate in B was 480×10^{-15} amp. On admitting $Zn(C_2H_5)_2$ at 6 mms. to the ionization chamber, the leak was now reduced to zero (certainly $< 1 \times 10^{-15}$ amp.). This shows that the $Zn(C_2H_5)_2$ absorbs all the light which causes Zn to emit electrons. Let us now calculate the leak to be expected in the $Zn(C_2H_5)_2$, assuming that the photo-electric properties of Zn are unchanged

* Pauer, *Wied. Ann.* LXI. p. 376.

by combination. The ratio of the light received by the ionization chamber to that received by the Zn plate is approximately

$$\left(8\frac{\pi(1{\cdot}9)^2}{11^2}\right) \div \left(4\frac{\pi(\cdot 2)^2}{(35)^2}\right) \doteq 2000.$$

The 8 and 4 refer to the lengths of the mercury arc seen from the ionization chamber and the zinc plate respectively. The expected leak is therefore $2000 \times 480 \times 10^{-15}$ amp. or $960{,}000 \times 10^{-15}$ amp.

With pure dry H_2 in the ionization chamber (at a potential of + 200 volts), the leak was 21500×10^{-15} amp.—the photo-electric current from the inner electrode. After evacuating the chamber and admitting $Zn(C_2H_5)_2$ at a pressure of 6 mms., the leak became too small to measure; it was certainly less than 2×10^{-15} amp., or at least 5×10^5 times less than that from a zinc surface receiving the same amount of light.

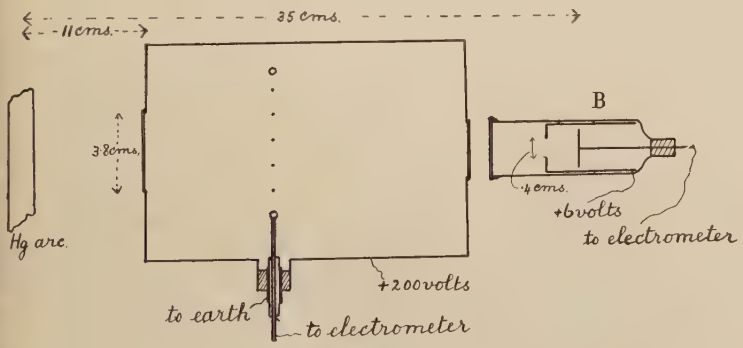


Fig. 1.

The ultra-violet light is totally absorbed by the $Zn(C_2H_5)_2$ in the one experiment and by the metallic zinc in the other. If any electrons had been emitted from the molecules of the vapour they would all have contributed to the ionization. On the other hand, it is certain that only a fraction of the electrons emitted from the molecules in the surface layer of the solid can get away from the surface, the majority of the electrons being absorbed. As we can only measure experimentally the number which emerge from the surface, it is clear that there is a large margin of safety when we say that the number of electrons emitted from the molecules of solid zinc is at least 5×10^5 times as great as the number emitted from the molecules of the vapour $Zn(C_2H_5)_2$, the same quantity of light being absorbed in both cases.

In view of some experiments (described later), in which most of the solid compounds tried were found to emit negative electricity when exposed to ultra-violet light, it was thought worth while

testing solid $Zn(C_2H_5)_2$. The apparatus is shown in fig. 2. As the mercury lamp could not be used in such a position as to send the light downwards, a reflector of quartz backed by mercury and tinfoil was made and mounted as shown. At the bottom of the tube was a thin sheet of zinc. The photo-electric leak (in vacuo) from this was small; the beam of light had to pass through rather narrow apertures to confine it to the zinc surface and probably a considerable amount of light was lost at the mirror. Enough $Zn(C_2H_5)_2$ was distilled from a side tube to cover the zinc sheet and then frozen by liquid air. (It was necessary to work with the substance at a low temperature on account of the absorbing power of the vapour.) There was now no measurable leak; a leak 100 times less than that from the Zn could have been detected. The apparatus was not sensitive enough to detect whether the solid $Zn(C_2H_5)_2$ surface possessed a real photo-electric effect less than 1 % of the effect for zinc.

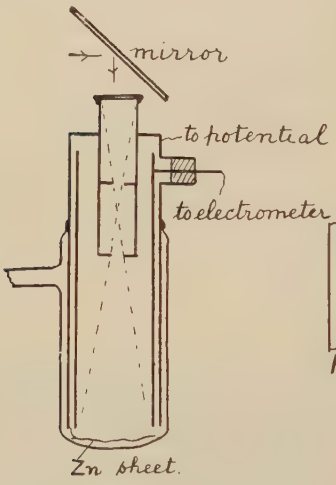


Fig. 2.

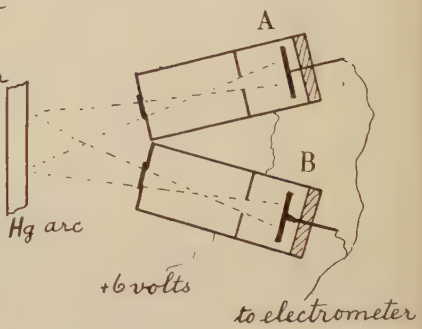


Fig. 3.

A preliminary experiment showed that $Zn(C_2H_5)_2$ had sufficient conductivity for the experiment. Two wires, the ends of which were 3 mms. apart, were dipped into the liquid and a potential difference of two volts applied. At ordinary temperatures, a current of 25×10^{-11} amp. was obtained, and at the temperature of liquid air the current fell to 8×10^{-11} amp.

Tin tetrachloride.

Experiments were carried out on $SnCl_4$ using the apparatus shown in fig. 1. When the apparatus was completely evacuated

and the case at +200 volts, there was a leak of $1{\cdot}5 \times 10^{-10}$ amp. (from the inner electrode) due to the light. On admitting $SnCl_4$, the leak became too small to measure (a leak of 2×10^{-15} amp. could have been detected). By altering the temperature of the liquid $SnCl_4$ in the side tube, different pressures of the vapour could be obtained in the apparatus. No leak was observed even when the liquid $SnCl_4$ was at its melting point. This illustrates the great absorbing power of $SnCl_4$ for the light which causes the carbon on the inner electrode to emit electrons.

The above results show that certain elements (C, Zn and Sn), when combined with other elements to form vapours, lose their power of emitting electrons when exposed to ultra-violet light. Some experiments were made on the effect of ultra-violet light on a number of solid compounds. In every case it was found that they were photo-electric, some giving nearly as large a current as the zinc. The results quoted below are only intended to exemplify this statement. Slight variations in the method of preparing the surfaces of the compounds were found to produce great differences in the photo-electric effect. Further experiments on these variations must be carried out in order to obtain reliable comparative figures for different compounds.

The apparatus is shown in fig. 3. A and B are two similar tubes. The leak from the Zn plate in A is used to standardize the light, and the Zn plate in B is covered with the compound to be tested. The leaks were always measured in a charcoal liquid air vacuum.

The photo-electric current from $ZnCl_2$ increased quite regularly as the surface became drier in the vacuum. The surfaces 1, 2, 7, 9 and 10 were prepared by dipping the Zn plate into the fused salt, a film of which immediately solidified on the surface. The surfaces 3, 4 and 6 were formed by heating the salt with or without a little water until the salt dissolved in its own water of crystallization. The Zn plate was then dipped into the liquid. Surfaces 8 and 9 were prepared by simply pressing the (chemically prepared) sulphide on the Zn plate.

The vapours CS_2, $Zn(C_2H_5)_2$, and $SnCl_4$, while showing no indication of ionization by ultra-violet light, strongly absorb the light which produces photo-electric effects in certain of their constituent elements. It is very probable that the absorption in the compound is due to that part which is photo-electric when uncombined, viz. C, Zn and Sn. In the case of the $Zn(C_2H_5)_2$, the H_2 is known to be perfectly transparent for all known wave lengths in the ultra-violet, and if the absorption is to be attributed to certain atoms in the molecule rather than to the molecule as a whole, then the absorption is due to the Zn and C.

If we consider that the least energy required for the removal

of an electron from a molecule is proportional to the smallest frequency which produces ionization, then the above results indicate that the electrons are more firmly attached to the molecules of the above vapours than to the photo-electric elements. A view has been put forward by Stark* that the electrons involved in the photo-electric effect are the valency electrons. When a metal enters into combination, more energy is required to remove the valency electron than before and hence shorter wave lengths are required to produce ionization. Reasoning on these lines, one might expect that the more stable the compound, the shorter is the wave length of the light required to produce a photo-electric effect. Yet we find that certain solid compounds of Zn ($ZnCl_2$ and $ZnSO_4$) are photo-electric, while the apparently less stable vapour $Zn(C_2H_5)_2$ cannot be ionized by the same light. The existence of a photo-electric effect in most of the solid compounds tried and its absence in the gaseous compounds suggest that an investigation might be made on the effect of ultra-violet light on the same substances when in the gaseous state and when in the solid state. An experiment on solid and gaseous $Zn(C_2H_5)_2$ was described above. It is proposed to continue the investigation in this direction.

Summary.

It has been shown that there is no trace of ionization in the vapours carbon bisulphide, tin tetrachloride and zinc ethyl when they are exposed to the ultra-violet light from a mercury arc. For the same amount of light energy, the leak from a zinc or carbon surface would be of the order 10^6 times that of the smallest effect which could be measured in these experiments.

I have pleasure in thanking Professor Sir J. J. Thomson for his interest in these experiments.

* Stark, *Phys. Zeit.* 1909, x. 787.

Compound	Photo-electric current (from Zn = 1)	Remarks on preparation of surface
1. $ZnCl_2$ (*a*)	·06 to ·08 (increasing regularly)	Surface wet after exposure to air before putting into apparatus
2. $ZnCl_2$ (*b*)	·24 to ·63 (increasing regularly for 20 hours)	Only a few minutes' exposure to air. Appeared quite dry
3. $ZnSO_4$ (*a*)	$\doteq$ ·6	Melted with addition of water
4. $ZnSO_4$ (*b*)	·12 to ·07	Melted without addition of water
5. ZnS	$\doteq$ ·07	
6. $SnCl_2$ (*a*)	$\doteq$ ·0016	Heated for short time until it became semi-fluid
7. $SnCl_2$ (*b*)	$\doteq$ ·12	Fused for a long time. Dark yellow in colour
8. PbS	·02	
9. KI	$\doteq$ ·5	Practically an insulator
10. NaOH ...	·93 to ·53 (decreasing regularly)	Surface appeared quite dry

On the Spores of some Jurassic Ferns. By H. Hamshaw Thomas, M.A., Downing College, Curator of the Botanical Museum, Cambridge.

[*Read* 8 May 1911.]

(Plate III.)

With the aid of a grant from the Gordon Wigan Fund, I have been investigating the fossil flora of the Jurassic Rocks of Yorkshire, and the object of this paper is to record the discovery of the spores and sporangia of two common Bathonian Ferns, *Coniopteris hymenophylloides* (Brongn.) and *Todites Williamsoni* (Brongn.). Further details with regard to these species will probably be given in papers which I hope to publish later.

Coniopteris hymenophylloides was first described by Brongniart* in 1828. It is particularly common in the Lower Estuarine Series exposed between Whitby and Hayburn Wyke, while fronds showing similar characters have been recorded from Poland, South Russia, Siberia, China, Japan, India, Virginia and Greenland. In several cases the fertile fronds with a much reduced lamina and a cup-shaped indusium have been figured, though the details of the sporangia and spores do not appear to have been hitherto described. Raciborski† has found fertile fronds on which the sporangia could be faintly distinguished, and Prof. Seward‡ has figured a drawing made by Dr Nathorst of a specimen of *C. quinqueloba* (Phill.), a closely allied species, in which a group of annulate sporangia are seen.

Last year I discovered a fertile specimen of this fern in the Lower Estuarine Shales at the top of Howdale Beck, Robin Hood's Bay, which was very well preserved (cf. fig. 1). No sporangia could be distinguished inside the indusium, but in the rock in which the specimen is embedded numerous remains of sporangia are seen. *Coniopteris hymenophylloides* is the only fern found in this bed and hence the specific identity of these sporangia with this species is rendered highly probable.

The sporangia are about ·4—·5 mm. long and tend to have a somewhat oblong shape. The annulus is very clearly seen and is composed of large cells (cf. figs. 2, 3). Though none of the specimens are quite perfect, there can be little doubt that the annulus was obliquely disposed. Sporangia of a very similar

* Brongniart, *Hist. Veg. Foss.*, p. 189, Pl. lvi. fig. 4, 1828.
† Raciborski, *Flora Kopalina Krakowskich*, Pl. iv. 1894.
‡ Seward, *Jurassic Flora Yorks.*, p. 114, Fig. 15, 1900.

shape and possessing an oblique annulus that can be closely compared with the Howdale specimens, are found in several modern representatives of the Cyatheaceae. In *Thyrsopteris elegans* Kze. they are somewhat similar in shape and are identical in size, while Diels* has also figured sporangia of *Hemitelia* which present a close agreement with my figures.

I have obtained specimens of spores from the Yorkshire example figured (fig. 1), but better preparations of these structures have been made from specimens from Kamenka, South Russia, which I have recently examined. One of these specimens is shown in fig. 4. By treating the contents of some of the sori with nitric acid and potassium chlorate, in the method recommended by Dr Nathorst, the remains of the spore-walls became clearly visible. As seen in figs. 5 and 6, the spores are small bodies about ·04 mm. in diameter and markedly tetrahedral in shape. They have a very delicate wall and show clearly the tetrad scar. They are almost identical in every respect with the spores of *Thyrsopteris elegans*, some of which are shown in fig. 7. Several other Cyatheaceous ferns possess similar spores.

The present observations lend considerable further support to the opinion which has been held for some time that *Coniopteris* is closely related to the modern Cyatheaceous ferns. Some authors have substituted the generic name of *Thyrsopteris* for that of *Coniopteris*, and while I have shown that the sporangia and spores of the two forms are very similar, yet they are probably also very like those of other Cyatheaceous forms and cannot be relied upon to support this conclusion.

Fertile fronds of *Todites Williamsoni* (Brongn.) from Yorkshire have long been known, and Schenk, Raciborski, and Zeiller have described the sporangia of closely allied species. A mass of the spores of this plant has been obtained and figured by Dr Nathorst† but no details can be made out from his figures. I believe that this is the first time that any details of the spores and sporangia have been made out from our English specimens.

I have recently obtained from the famous Gristhorpe Bay plant-bed several very fine specimens of this plant. A number of them show fertile pinnae with sporangia almost completely covering the backs of the pinnules. Some of the sporangia are fairly well preserved, they are ·3—·4 mm. in diameter, being about half the size of the sporangia of *Todea barbara*. They appear to have been exannulate; the wall of the sporangium consisted of a network of somewhat thickened cells radially arranged round a group of smaller cells which seem to occupy the apex (fig. 8). No very

* Diels in Engler and Prantl, *Pflanzenfamilien*, Vol. I. 4, p. 130, fig. 82 D.

† Nathorst, *Palaeobot. Mitteilungen*, 4. *K. Svenska Vet. Acad. Hand.*, Bd 43, No. 6, Taf. 1, fig. 7, 1908.

satisfactory specimen of a sporangium which has dehisced was recognised, though Zeiller* has figured such specimens, in which the line of rupture is lateral. It is clear from the examination of these sporangia that they differed somewhat from those described by Raciborski and also from those of the modern *Osmundaceae*, for they appear to have a group of cells with walls of uniform thickness, regularly arranged round the apical part of the sporangium, and not a small group of thickened cells laterally placed.

Since this paper was first written Dr T. G. Halle has shown to me the results of his examination of some fertile specimens of *Cladophlebis denticulata*. The sporangia of this form are pear-shaped bodies and appear to possess a cap of thick-walled cells covering their apical portion and more or less radially arranged. These sporangia if viewed from above would present an almost identical appearance with those of my Gristhorpe *Todites*, and on closer examination of the latter by Dr Halle's method, I have also seen indications of thinner-walled cells in their basal region. In his paper† Dr Halle points out that his sporangia differ markedly from those of the modern *Osmundaceae* and also from those previously figured as *Todites*, he therefore has given his specimens the new generic name of *Cladotheca*. But though they differ from the *Osmundaceae*, as he points out, yet they are doubtless closely allied to the English *Todites*, and it is doubtful whether the difference in the arrangement of the sporangia on the pinnules is a sufficient ground for separating off this new genus *Cladotheca* from *Todites*.

When some of the sporangia of *Todites* are removed and treated with the clearing solution, the spores which they contained become clearly visible. Since the spores adhere closely together it is rather difficult to make out even the approximate number which was produced in each sporangium, but it appears to have been of the order of 100. The individual spores are about ·06 mm. in diameter; they show a thick cuticular wall, and possess a much darker brownish colour than the spores of *Coniopteris*. The wall may have been slightly sculptured. They are usually crushed so as to give the appearance of a spindle-shaped fold in their interior, but though this fold is seen in most of the spores its significance is not clear. In many cases the tetrad marking can be seen to be formed of three fine lines; it is not so conspicuous as in *Coniopteris*.

On comparing these spores with those of the modern *Todea barbara*, several points of resemblance are noticeable. The modern spores are spherical bodies of about the same diameter (·05 mm.)

* Zeiller, *Flore. Foss. Tonkin*, p. 42, Pl. III. figs. 1*c—f*, 1902.

† Halle, On the fructifications of Jurassic fern-leaves of the *Cladophlebis denticulata* type, *Arkiv för Botanik, K. Sv. Vet. Acad.* Bd 10, No. 15, 1911.

with a rather thick and slightly sculptured exospore. They also have a fine tetrad scar.

The spores therefore provide further points of resemblance between the Jurassic and the modern genus.

Specimens have also been found in Yorkshire showing the sporangia of *Laccopteris polypodioides* and *Matonidium Goepperti*, which show similar characters to those already figured by Schenk* and Prof. Seward†. Some specimens of separate pinnules probably of *Cladophlebis lobifolia* (Phill.) have also been found in the Gristhorpe Bed. One of these was in a fertile condition, each of the pinnules bearing several small sori. There is a similar fertile specimen in the Naturhistoriska Riksmuseum at Stockholm, which was collected in Yorkshire by Prof. Nathorst some time ago, which is probably the example figured by Prof. Seward in his Jurassic Flora‡. The lamina of the fertile pinnules is slightly reduced and small swellings are seen at the edges of four or five of the lobes. Each of these was a sorus completely covered by an indusium, and very similar in appearance to those of the modern *Dicksonia antarctica*§. No sporangia have yet been seen attached to the fronds, but small annulate sporangia were seen in the matrix near the pinnae and might possibly have belonged to this species. One of the sori of the Stockholm specimen was removed and treated with acid, and a large number of small spores were then seen. These were about ·04 mm. in diameter, tetrahedral in shape and had the usual tetrad scar marking (see text-figure).

Spores of *Eboracia lobifolia*. ×200.

It was at once noticeable that, in their form and appearance, these spores showed a much greater resemblance to those of Coniopteris and the Cyatheaceae than to those of Todites and the Osmundaceae.

The occurrence of these sori and spores makes it now possible for us to remove *Cladophlebis lobifolia* from the old form genus

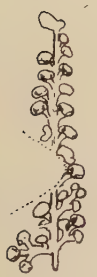
* Schenk, *Flora Nordwestdeutschen Wealdenformation, Palaeontographica*, 1875.
† Seward, *Jurassic Flora Yorks.*, p. 85, fig. 11, 1900.
‡ *Ibid.*, p. 149, fig. 23.
§ Raciborski has figured similar specimens under the name of *Dicksonia lobifolia*. *Pamiet. Mat. przy. Akad. Umiej.* Pl. xii figs. 1—3, 5—6, 1894.

Cladophlebis, which is associated to some degree with the Osmundaceae. There are not sufficient grounds for placing it in the genus *Dicksonia*, as Raciborski has done; and while it is related in the character of its sori and spores to Coniopteris, yet the form of the fertile fronds is very distinct. It may be provisionally placed in a new genus *Eboracia**, but the fuller description of this genus will be reserved until more material has been obtained.

Explanation of Figures on Plate III.

Fig. 1. Part of fertile frond *C. hymenophylloides* from Howdale, $\times \frac{3}{2}$. Figs. 2, 3. Sporangia of same, × 38. Fig. 4. Fertile frond from Kamenka, × 2. Fig. 5. Separate spores from this specimen, × 230. Fig. 6. Group of spores, × 230. Fig. 7. Spores of *Thyrsopteris elegans*, × 230. Fig. 8. Sporangia of *Todites Williamsoni*, × 35. Fig. 9. Spores of same, × 230.

* It was first found in the county of which York (Lat. Eboracum) is the capital.



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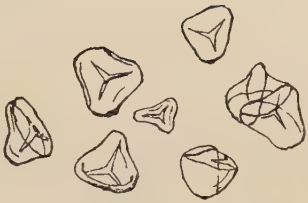

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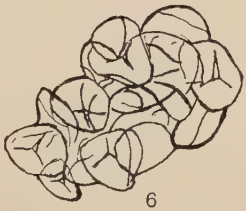

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The Discharge of Spermatozoa by Unio pictorum.

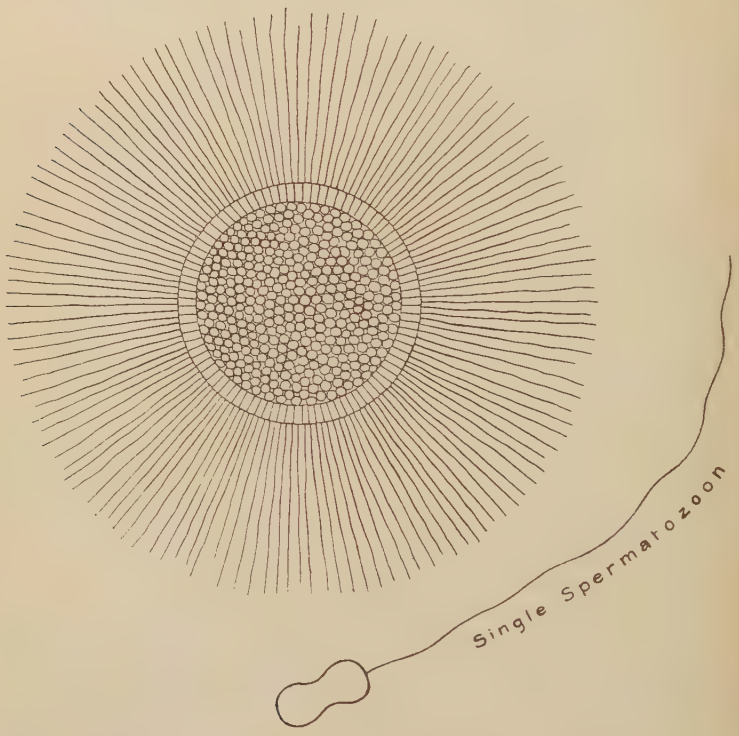
By Oswald H. Latter. (Communicated by Dr Shipley.)

[*Received* June 1, 1911.]

I am not aware that this phenomenon has ever been witnessed in circumstances so favourable as fell to my lot on the morning of May 18th, 1911. On the previous day I had transferred the mussel from an aquarium, which has always been replenished with ordinary tap-water, to another that had recently been provided with fresh river-sand and filled up with rain-water for the accommodation of some toad tadpoles. On entering the laboratory shortly before 8 a.m. on the 18th I at once perceived that the *Unio* had journeyed all round the aquarium, travelling between three and four feet, and had come to rest close against an *Anodonta*, which I had introduced at the same time. A closer inspection revealed a fine double stream of milky substance issuing rapidly from the exhalant aperture, rising nearly to the surface, and then falling as a diffused cloud. The two streams were slightly divergent, and both somewhat obliquely directed in an anterior direction. The amount of material emitted was so great that the whole of the water in the aquarium, measuring 2 ft. 6 in. in length, 10 in. in width and filled to a depth of about 7 in. with water above the sand, was very soon rendered cloudy throughout. The phenomenon continued for some hours and had not entirely ceased at 12.30 p.m. The emission appeared to be under control, for a slight shaking of the floor was followed by a cessation of the streams, though the ordinary exhalant current of water appeared to continue without interruption.

I secured samples of the ejected matter and found it to consist of myriads of spherical spermatophores, measuring about ·02 mm. in diameter. The heads of the spermatozoa formed the periphery of the sphere, and beyond these projected the very long and actively vibratile tails which by their lashing movements caused the spermatophores to revolve and swim along after the fashion of a *Volvox*. The length of the cilia was fully equal to that of the diameter of the spermatophore. There appeared to be some repulsion between the individual spermatophores; for if two came within range of one another in the field of the microscope, they speedily moved apart in opposite directions. In the course of a few hours the spermatophores began to break up into component spermatozoa. These last on becoming free from their fellows exhibited the most astonishing activity, darting here and there with such speed that, under a $\frac{1}{6}$ objective and No. 2 eyepiece, there was some difficulty in retaining an individual specimen within the field of view. Their vitality was in no degree impaired at the end of seven hours after quitting the parent mussel, in

spite of the unfavourable circumstance of confinement between the cover-slip and slide. The head of each spermatozoa exhibited a very definite transverse constriction, rendering it like a dice-box in shape. For several of these observations I am indebted to my pupil G. K. G. Keen, and also for the accompanying illustrations which may render the above account more clear. I have preserved a number of the spermatophores in 100 °/₀ alcohol and shall be pleased to place them at the disposal of any one to whom they may be of value.



*The non-nitrification of sewage in sea-water**. By J. E. Purvis, M.A., A. C. N. M^{c}Hattie and R. H. J. Fisher.

[*Read* 22 May 1911.]

Systematic chemical and bacterial investigations on the decomposition of sewage in sea water have been described in researches previously published by Messrs Purvis, Coleman, Courtauld, Macalister and Minett†. The results proved that sewage undergoes very slow decomposition in sea water: and the primary cause appears to be the rapid destruction of the nitrifying organisms.

In order to meet the criticism that the method of incubation partially eliminated the oxygen necessary for the growth of the nitrifying organisms, the authors have passed dry air, and containing no CO_2, through various mixtures of sewage and sea water for over seven weeks. The mixtures were examined from time to time for the two ammonias and for nitrites and nitrates. Neither nitrites nor nitrates were found at any time, and the total ammonia was only slightly decreased.

The results confirm the earlier researches and shew that, even when abundant oxygen is there, no nitrification occurs in sewage when mixed with sea water.

* A detailed account of this investigation appears in the *Jour. Roy. San. Inst.* (1911), vol. xxxii. p. 442.

† *Jour. Roy. San. Inst.* (1906), vol. xxvii. p. 433; *Proc. Camb. Phil. Soc.* vol. xv. p. 354; *7th Int. Congress of Applied Chemistry* (1909), Sect. VIII *a*, p. 272.

PROCEEDINGS AT THE MEETINGS HELD DURING THE SESSION 1910—1911.

ANNUAL GENERAL MEETING.

October 31*st*, 1910.

In the Cavendish Laboratory.

PROF. HOBSON, VICE-PRESIDENT, IN THE CHAIR.

The following were elected Officers for the ensuing year:

President:

Prof. Sir George Darwin.

Vice-Presidents:

Dr Fenton.
Prof. Seward.
Prof. Newall.

Treasurer:

Prof. Hobson.

Secretaries:

The Master of Christ's.
Dr Barnes.
Mr A. Wood.

Other Members of the Council:

Mr W. E. Dixon.
Prof. Wood.
Prof. Hopkinson.
Mr G. H. Hardy.
Prof. Sir J. Larmor.
Prof. Biffen.
Prof. Pope.
Mr R. H. Rastall.
Mr K. Lucas.
Mr E. A. Newell Arber.
Prof. Sir J. J. Thomson.
Mr J. E. Purvis.

The following were elected Associates:

J. L. Glasson, Gonville and Caius College.
A. E. Oxley, Trinity College.

The following Communications were made:

1. A new method of investigating the positive rays. By Professor Sir J. J. Thomson.

2. Preliminary note on the properties of easily absorbed Röntgen Radiation. By R. Whiddington, B.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

3. The Ionisation of Heavy Gases by X-rays. By R. T. Beatty, B.A., Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

4. The Mobility of the Positive Ion in Flames. By S. G. Lusby. (Communicated by Professor Sir J. J. Thomson.)

5. Mobility of the Positive Ions in gases at Low Pressures. By G. W. Todd. (Communicated by Professor Sir J. J. Thomson.)

6. Fourier's double integral and the theory of divergent integrals. By G. H. Hardy, M.A., Trinity College.

November 14*th*, 1910.

In the School of Agriculture.

Professor Wood in the Chair.

The following was elected a Fellow of the Society:

W. B. Alexander, B.A., King's College.

The following were elected Associates:

E. A. Owen, Trinity College.
J. C. Wasson, Trinity College.

The following Communications were made:

1. Some crosses with Rivet wheat. By Professor Biffen.

2. On the inheritance of the yellow factors in sweet pea colouring. By Mrs D. Thoday and D. Thoday, M.A., Trinity College.

3. Demonstration of Mendelian Laws of Heredity in the Potato. By Dr R. N. Salaman.

4. The feeding value of Mangels. By Professor Wood.

5. Some causes of Sterility in Cattle. By F. H. A. Marshall, M.A., Christ's College.

6. Caponising. By F. H. A. Marshall, M.A., Christ's College, and K. J. J. Mackenzie, M.A., Christ's College.

7. Notes on Protein hydrolysis. By F. W. Foreman, B.A., Gonville and Caius College. (Communicated by Professor Wood.)

November 28th, 1910.

In the Chemical Laboratory.

PROFESSOR SIR GEORGE DARWIN, PRESIDENT, IN THE CHAIR.

The following were elected Fellows of the Society:

C. C. Mason, M.A., Trinity Hall.
P. J. Daniell, B.A., Trinity College.

The following was elected an Associate:

F. H. Hatch.

The following Communications were made:

1. Demonstration of Natural Colour Photography of Interference Figures. By Professor POPE.

2. (1) Colloidal form of Nastvogels' osazone. (2) A method of characterising certain Ureides. By Dr FENTON and W. A. R. WILKS, B.A., Gonville and Caius College.

3. The Racemisation of Malic and Tartaric Acids by Heat. By H. O. JONES, M.A., Clare College, and D. I. JAMES, B.A.

4. A note on the action of aluminium chloride on benzene. By Miss A. HOMER.

5. Some theorems concerning uniform functions of two complex variables together with some simple properties of such functions. By Dr FORSYTH.

6. Note on the Fundamental Theorem of Integration. By Dr YOUNG.

7. (1) The Determination of the Exponent to which a number belongs, the Practical Solution of certain Congruences, and the Law of Quadratic Reciprocity. (2) The Divisors of certain Arithmetical Forms, the Primes of certain Forms, and the arrangement of Quadratic and some other Residues. By H. C. POCKLINGTON, M.A., St John's College.

8. Note on Spermatogenesis of *Abraxas grossulariata*. By L. DONCASTER, M.A., King's College.

9. The discharge of positive electricity from sodium phosphate heated in different gases. By F. HORTON, M.A., St John's College.

10. On the distribution of Secondary Röntgen Radiation round a radiator. By J. A. CROWTHER, M.A., St John's College.

11. The radium content of salts of Potassium. By J. SATTERLY, B.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

January 23rd, 1911.

In the Optical Lecture Room.

Professor Sir George Darwin, President, in the Chair.

The following Communications were made:

1. (1) A constant temperature, porous plug experiment. (2) Observations on the Surface Tension of Liquid Sulphur. By W. A. D. Rudge, M.A., St John's College.

2. On the magnetic susceptibilities of certain compounds. By A. E. Oxley. (Communicated by Professor Sir J. J. Thomson.)

February 6th, 1911.

In the Optical Lecture Room.

Professor Hobson, Treasurer, in the Chair.

The following Communications were made:

1. On the Distribution of the *Megapodidae* in the Pacific. By J. J. Lister, M.A., St John's College.

2. Note on *Strongylocentrotus lividus* as a Rock-borer. By J. Romanes, B.A., Christ's College.

3. Exhibition of sketches of a peculiar tracheal system of a *Mycetophilous* larva (Diptera). By A. J. Grove. (Communicated by Mr H. Scott.)

February 20th, 1911.

In the New Medical Schools.

Professor Sir George Darwin, President, in the Chair.

The following Communications were made:

1. The adaptation of ticks to the habits of their host. By Professor Nuttall.

2. The entry of bacteria into the lungs. By Dr Cobbett and Dr Graham-Smith.

3. The action of caffeine on muscle. By Dr F. Ransom. (Communicated by Mr W. E. Dixon.)

4. Toleration to nicotine. By W. E. Dixon, M.A., Downing College.

5. The action of pituitary extract and adrenalin on peripheral arteries. By Dr Cow. (Communicated by Mr W. E. Dixon.)

6. The action of ultra-violet rays on blood sera. By W. M. Scott. (Communicated by Professor Woodhead.)

7. The scattering of X-Rays. By E. A. Owen. (Communicated by Professor Sir J. J. Thomson.)

March 13th, 1911.

In the Cavendish Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following Communications were made:

1. Exhibition of Photographs of Kanal Strahlen. By Professor Sir J. J. Thomson.

2. (1) Freezing Point and Depression of Freezing Point of Sodium Chloride. (2) A Simple form of Electric Resistance Furnace. By F. E. E. Lamplough, M.A., Trinity College.

3. Some Experiments on Scattered Röntgen Radiation. By J. A. Crowther, M.A., St John's College.

4. On Regularities in the Spectrum of Neon. By H. E. Watson. (Communicated by Professor Sir J. J. Thomson.)

5. Fatigue and Persistence Effects in the Production of Secondary Röntgen Rays. By J. C. Chapman. (Communicated by Professor Sir J. J. Thomson.)

6. The absorption spectra of the vapours of some sulphur compounds. By J. E. Purvis, M.A., St John's College.

7. Intensity of Secondary Homogeneous Röntgen Radiation from Compounds. By J. C. Chapman and E. D. Guest. (Communicated by Professor Sir J. J. Thomson.)

May 8th, 1911.

In the Botany School.

Professor Seward, Vice-President, in the Chair.

The following Communications were made:

1. On the spores of some Jurassic Ferns. By H. Hamshaw Thomas, M.A., Downing College.

2. On a new species of Salicornia from Angola. By C. E. Moss, B.A., Emmanuel College. (Communicated by Professor Seward.)

3. On the detection of Maltose in the tissues of certain Angiosperms. By S. Mangham, B.A., Emmanuel College. (Communicated by Professor Seward.)

May 22nd, 1911.

In the Chemical Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following was elected an Associate:

E. Jacot.

The following Communications were made:

1. Attempts to resolve asymmetric Nitrogen Compounds of low Molecular Weight. By Professor Pope and J. Read.

2. "Aldehydo-glyceric" acid. By Dr Fenton and W. A. R. Wilks, M.A., Gonville and Caius College.

3. Triketohydrindene Hydrate. By S. Ruhemann, M.A., Gonville and Caius College.

4. The non-nitrification of sewage in sea-water. By Messrs J. E. Purvis, M^{c}Hattie and Fisher.

5. Complex thio-oxalates. By H. O. Jones, M.A., Clare College, and C. S. Robinson, B.A., Emmanuel College.

6. Further Experiments on Scattered Röntgen Radiation. By J. A. Crowther, M.A., St John's College.

7. The Production of characteristic Röntgen Radiations. By R. Whiddington, B.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

8. On the Velocities of the Electrons produced by Ultra-Violet Light. By A. Ll. Hughes, B.A., Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

9. (1) The Origin of spectra. (2) On the positive ionisation produced by phosphates when heated. By F. Horton, M.A., St John's College.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

Preliminary Note on the Characteristic Homogeneous Röntgen Radiation from Elements of High Atomic Weight. By J. Crosby Chapman, B.Sc., Research Student of Gonville and Caius College, Cambridge, Layton Research Scholar of the University of London, King's College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 13 November 1911.]

In a recent paper* in the *Philosophical Magazine*, Professor Barkla has published a complete list of those elements which, up to the present, have been shown to emit the characteristic Röntgen radiation or as he called it the "fluorescent" radiation. If the relation between the atomic weight and $\frac{\lambda}{\rho}$, where λ is defined by the equation $I = I_0 e^{-\lambda x}$ and ρ is the density of Al for the characteristic radiations of the various elements be plotted taking atomic weight as abscissae and $\frac{\lambda}{\rho}$ as ordinates, then the points corresponding to the elements with atomic weights between calcium and cerium lie on an approximately smooth curve. If however the elements with higher atomic weights than silver are examined under suitable conditions, it becomes evident that there are with these elements two types of characteristic radiation, one the hard homogeneous radiation such as the first curve would suggest, and superposed on this a soft radiation. Barkla and Nicol† have investigated the soft radiation from the elements antimony, iodine and barium and have shown that these elements emit in addition to the ordinary characteristic radiation, another soft radiation which is also characteristic of the element and moderately homogeneous. Although no detailed results have as yet been published the values of $\frac{\lambda}{\rho}$ for these elements have been given and when these are plotted on the same diagram a second curve is obtained. When this curve is continued towards the x axis it is obvious that, if it resembles in form the first curve (Ca-Ce), it will pass through

* *Phil. Mag.* Sept. 1911. † *Nature*, Aug. 4, 1910.

the region of atomic weights between 184 and 208, which contains tungsten, gold, platinum, lead and bismuth. Up to the present, these five elements have not been investigated as regards their power of emitting a characteristic homogeneous radiation. To examine whether the radiation from this second series is similar to that from the first series, the radiation from lead, which is a typical member of the second series, was examined in detail.

The difficulty encountered with the elements in the second group when investigating the type of rays emitted, is that a considerable amount of the incident primary radiation is simply scattered, without being converted into the fluorescent radiation which it is desired to investigate. So that unless the scattered radiation is, by some means, allowed for and subtracted, the presence of the homogeneous constituent tends to be completely masked.

The usual apparatus was employed with slight modifications in order to be able to allow for the scattering effects. The method of subtracting the merely scattered radiation was, roughly, as follows: a very hard bulb was used with an equivalent spark gap of five to six inches, as the source of the X-rays, and the primary rays were made to pass through a thick sheet of Al in order to cut off any but the hardest constituents of the beam. This penetrating primary was allowed to fall on a thin sheet of lead foil. The thickness of this sheet was just more than sufficient to allow the layer to be considered as an infinitely thick sheet for the homogeneous radiation, while owing to the small mass of the lead present the intensity of the scattered radiation was reduced to a minimum. The rays leaving the lead consisted of: (1) the homogeneous constituent, (2) the superposed scattered constituent. This heterogeneous radiation was then examined by finding the absorption by successive sheets of Al of the same thickness; the effect of putting in an aluminium sheet in the path of the radiation, is to cut down the homogeneous constituent, while owing to the great hardness of the scattered constituent, the latter is not cut down appreciably. So that if a sheet of Al sufficient to completely cut off the whole of the homogeneous constituent be put in front of the electroscope it is possible to find the total amount of scattered radiation, for, provided the primary is kept hard enough, the scattered, which is of the same degree of hardness, is not appreciably absorbed even by an Al sheet sufficient to cut off the whole of the homogeneous constituent. The absorption of the whole of the radiation by Al was first measured in the ordinary way, then the amount of scattered radiation was determined, and as this is a constant factor entering into all the previous readings it could be subtracted leaving values from which the absorption of the homogeneous constituent alone

could be found. The apparatus and a more detailed account of this correction will be described in a later paper.

The following were the results obtained.

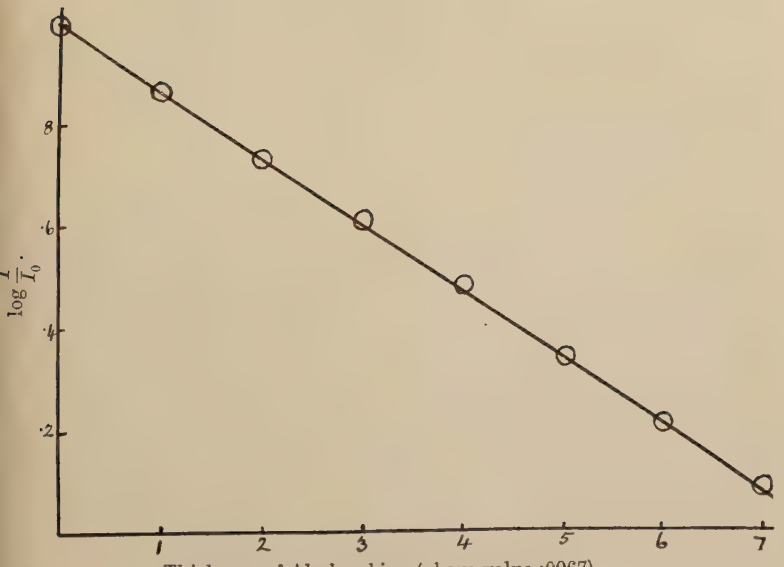
TABLE I. *Results for lead radiation.*

Percentage absorption in Al previous to absorption in column II	Percentage absorption by Al (·0067 cm.) after absorption in column I
12	25·6
35	26·3
52	25·8
65	25·8
74	27·8
81	26·0
86	26·1

Mean value of percentage absorption by Al (·0067 cm.) = 26·2.

$$\frac{\lambda}{\rho} = 17{\cdot}4.$$

CURVE I.



If now Curve I is plotted showing the relation between $\log \frac{I}{I_0}$ and x, where $I = I_0 e^{-\lambda x}$, taking $\log \frac{I}{I_0}$ as ordinate and x the thickness of aluminium absorbing as abscissa, the almost complete homogeneity of the radiation exhibits itself in the straight line which indicates that the beam is being absorbed exponentially.

That is lead which was taken as a typical member of the second group of elements emits under suitable conditions a characteristic radiation, and this radiation has been shown to be almost perfectly homogeneous when the experiment is performed in a manner which allows the scattered radiation to be subtracted.

Selective absorption by lead.

The other characteristic of elements in the first group is that they show a selective absorption for radiations which have a penetrating power just greater than their own. Thus if the coefficient of absorption of an element X which gives a characteristic radiation be measured for the various homogeneous radiations from silver to chromium, beginning with a very soft homogeneous radiation the absorption is considerable; as the radiation is made more penetrating the absorption in Al and the element X diminish proportionately, but when the radiation which is being absorbed is made more penetrating than the secondary radiation characteristic of the metal X the absorption first ceases to diminish as rapidly as the absorption in Al, then it increases, at this point the characteristic radiation of X is excited. As the beam becomes more penetrating the absorption in the element begins to diminish and again the absorption in Al and the metal diminish proportionately.

In order to show that the same phenomenon takes place in lead, an even layer of lead oxide (Pb_3O_4) was used as the absorbing screen, since it is difficult to obtain lead in thin enough sheets to be used for this purpose. It will be seen that the absorption by the oxygen in the lead oxide will be almost negligible when the relation between the weight of lead and oxygen in the compound and their respective absorption coefficients are considered. In this way it is possible to calculate the value of the relative absorption coefficient by lead $\left(k\frac{\lambda}{\rho}\right)$ for the various homogeneous radiations. The series of homogeneous beams of the first group used were copper, zinc, arsenic, selenium, bromine, strontium, molybdenum, silver, tin. The percentage absorption by the lead oxide was found for each of these radiations and from the values

obtained the relative value for $\frac{\lambda}{\rho}$ in lead was calculated for each particular beam.

The results are given below.

TABLE II. *Absorption by lead and aluminium.*

Secondary Radiator	Absorption in Al $\left(\frac{\lambda}{\rho}\right)$	Absorption in Pb $\left(k\frac{\lambda}{\rho}\right)^*$	$\frac{\text{Absorption in Pb}}{\text{Absorption in Al}}$ (=1/k times value below)
Copper	47·7	269	5·6
Zinc	39·4	224	5·7
Arsenic	22·5	140	6·2
Selenium	18·9	129	6·9
Bromine.....	16·4	126	7·7
Strontium	13·0	161	12·4
Molybdenum...	4·7	143	30
Silver..	2·5	84	34
Tin.....	1·57	63	40

* k is of order unity.

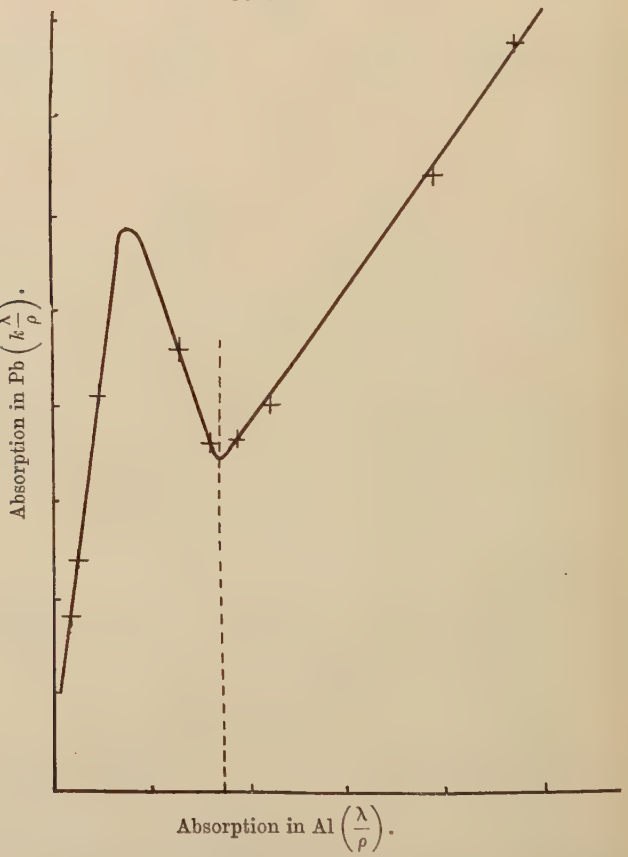
The values obtained above are plotted in Curve II which shows the relation between the absorption in Al and the relative value of absorption in lead.

The value obtained for the $\frac{\lambda}{\rho}$ in Al for lead radiation is 17·4, the value for selenium is 18·9 and that for bromine 16·3; so that if the homogeneous radiation emitted by lead has the same properties as those shown by elements in the Cr-Ce group, we should expect that the selenium would just be unable to excite the characteristic lead and that bromine would just be able to stimulate it; so that the curve showing the relation between the absorption in Al and the relative absorption in lead should commence to rise between selenium and bromine, and from an examination of the curve this will be found to be the case. The dotted line shows the point at which the homogeneous lead radiation is excited if it obeys the same laws as the first group.

The results of these experiments show that lead though belonging to a different group of elements with reference to their

power of emitting secondary characteristic Röntgen radiation, yet superposed on the scattered radiation, they do at all times, if the primary beam is sufficiently penetrating, give out an almost perfectly homogeneous radiation, and as regards absorption phenomena lead behaves in a similar manner to the elements in the

CURVE II.



first group. The results discussed above would certainly go to show that the mechanism of the production and that the type of radiation is the same for elements in the second group as for those in the first. This research is being continued, using the other elements of the second group—tungsten, gold, platinum and bismuth.

My thanks are due to Sir J. J. Thomson for his interest in this experiment.

Note on the condensation of tryptophane with certain aldehydes. By Miss Annie Homer, Beit Memorial Research Fellow. (Communicated by Mr F. G. Hopkins.)

[*Read* 27 November 1911.]

The following investigation arose from an attempt to prepare oxidation and reduction products of tryptophane.

The ordinary methods of oxidation, other than the ferric chloride method used by Hopkins and Cole (*Journ. Physiol.* xxix. 464), failed to give crystalline products. But when repeating the work of these authors, I failed, as Ellinger had (*Ber.* xxxix. 2, 2515), to isolate any of the interesting base, $C_{12}H_{10}N_2$. In this connexion Dr Hopkins had made the observation that a crystalline derivative formed when tryptophane was in contact with moist ether which had been locally heated with a glass rod. This compound proved not to be the base $C_{12}H_{10}N_2$. At his suggestion I investigated the properties of the new substance.

The crystalline compound was of an acidic nature. It was slightly soluble in water and in alcohol; dissolved in sodium carbonate solution with the evolution of carbon dioxide and was reprecipitated by dilute acids; was not attacked by dilute acids or by mild alkalis, but was decomposed by concentrated acids and caustic alkalis. It melted at 322° C. This substance will be referred to as the ether oxidation substance.

Analyses gave results in accordance with the following formulae:

(*a*) Dried at 20°, $C_{24}H_{26}N_4O_5 . 2H_2O$.
(*b*) Dried at 110°, $C_{24}H_{26}N_4O_5$.
(*c*) Heated to 150°—200°, $C_{24}H_{24}N_4O_4$.

The loss of H_2O in the change from (*b*) to (*c*) is due to a molecular change and not to loss of water of crystallisation.

Now by the local heating of moist ether there are evolved pungent fumes in which hydrogen peroxide and formaldehyde can be detected. The former has probably arisen from the first formed peroxides of ether which, in contact with water, are decomposed with the liberation of hydrogen peroxide (Berthelot, *C. R.* 108, 543; Dunstan and Raymond, *J. C. S. Trans.* 1890, 75).

I found that hydrogen peroxide would not react with tryptophane; formaldehyde and certain aldehydes would. The question arose as to whether the ether oxidation substance was a formaldehyde derivative of tryptophane or not.

The *formaldehyde* compound melted and decomposed at 235°—240°. It was readily hydrolysed by water, dilute acids

and alkalis to form the ether oxidation substance. During hydrolysis formaldehyde was also liberated. It evidently differs from the ether oxidation substance in that it is a methylene type of compound, but at the same time there is some close relationship since hydrolysis readily converts the formaldehyde derivative into the ether oxidation substance.

Analyses gave results in accordance with the following formulae:

Dried at 20°, $C_{12}H_{12}N_2O_2 . 2H_2O$.

Dried at 110°, $C_{12}H_{12}N_2O_2 . H_2O$.

Heated to 150°, decomposition began to take place.

By the action of *glyoxylic acid* on tryptophane in aqueous solution, a crystalline derivative was formed. The substance melted at 322° and when mixed with some of the ether oxidation substance the melting point was unchanged. It was moderately soluble in hot water and alcohol; readily soluble in alkalis, but on acidification of the alkaline solution with acetic acid the acid sodium salt and not the free acid was precipitated.

Analyses gave results in accordance with the following formulae:

(*a*) For the free acid, $C_{13}H_{11}N_2O_4$.

(*b*) For the acid sodium salt, $C_{13}H_{10}N_2O_4Na . 4H_2O$.

When the free acid was heated to 205° carbon dioxide was evolved, and the residual substance had a percentage composition in accordance with the formula of the ether oxidation substance heated above 150°, viz. $C_{24}H_{24}N_4O_4$.

There is thus an interesting connexion between these products. The ether oxidation substance is the most stable of the three; it is formed from the formaldehyde compound by hydrolysis and from the glyoxylic derivative by the action of heat. The question as to the constitution of these derivatives cannot be approached in a preliminary note, but the special interest that they afford with reference to the Adamkiewicz reaction may be touched upon.

In the Adamkiewicz reaction glyoxylic acid is regarded by Hopkins and Cole, *loc. cit.*, as the substance essential to the formation of the characteristic violet colour. Rosenheim (*Biochem. J.* 1906, 1. 233—240) points out that the colour produced by the action of formaldehyde on proteids in presence of sulphuric acid and oxidising agents (Voisenet, *Bull. Soc. Chim. Paris* (3) 33, 1198) is identical with that produced in the Adamkiewicz reaction. He criticises Hopkins and Cole's view as to the importance of glyoxylic acid *per se*; he suggests that even with glyoxylic acid the presence of an oxidising agent is essential and that, although an oxidising agent may not have been added, yet the glyoxylic acid itself, however carefully prepared, is always

contaminated with sufficient hydrogen peroxide for the reaction to be possible.

The isolation of the three compounds described above and an investigation of their properties afford evidence in favour of the essential factor being formaldehyde.

Colour reactions produced by the action of concentrated sulphuric acid on the products described above.

Action of concentrated sulphuric acid	Formaldehyde product	Glyoxylic product	Ether oxidation substance
A. On the solid—			
i. in the cold	Violet	Yellow	None
ii. on warming	Colour intensified. Finally charring	Colour intensified. Finally charring	Slight violet tint
B. On the solid suspended in water—			
i. directly treated with the acid	Violet	Yellow	None
ii. heated to 90°, cooled and then treated with the acid	Violet colour intensified	Yellow	None
iii. in the presence of a trace of formaldehyde	Violet colour intensified	Violet	Violet
iv. in the presence of a trace of glyoxylic acid	Violet	Violet	Violet
v. in the presence of a trace of ferric chloride	Very intense bluish violet colour	Brown	Green
vi. in the presence of a trace of hydrogen peroxide	Brown	Claret	Brown

From the above table it is obvious that formaldehyde plays an important part in the colour reaction, since, of the three products, the only one which will give the colour without the addition of glyoxylic acid or formaldehyde, is the formaldehyde condensation product. It has been shown that this product is hydrolysed by water with the liberation of formaldehyde, and after this process (B ii) the colour reaction is more marked still.

Were the essential factor glyoxylic acid *per se*, then the glyoxylic condensation product ought to give the colour reaction with sulphuric acid, but it will not do so unless formaldehyde

or more glyoxylic acid be added. Now glyoxylic acid itself is decomposed by sulphuric acid with the formation of carbon dioxide and formaldehyde. It therefore seems reasonable to assume that glyoxylic acid is able to take part in the colour reaction by virtue of its decomposition into formaldehyde, and not, as Rosenheim suggests, because of contamination with hydrogen peroxide. The fact that the colour reaction is not given by glyoxal and glycollic aldehyde, neither of which give formaldehyde on treatment with acid, is in support of this view.

It will be noticed that in these experiments formaldehyde has been used unaccompanied by an oxidising agent, but when testing for tryptophane by means of formaldehyde it is customary to add a trace of an oxidising agent, otherwise the characteristic colour is not obtained. Now tryptophane when acted upon by concentrated sulphuric acid and formaldehyde is readily charred, but, unless the temperature be raised or excess of formaldehyde be used, there is no such effect in the case of the condensation products described in this paper. I found that if the aqueous solution of tryptophane to which a few drops of formalin had been added, were first heated, cooled, and then treated with the concentrated acid, then the characteristic violet colour was produced. It is obvious that in testing for the presence of tryptophane with formaldehyde the addition of an oxidising agent is unnecessary, but the conditions for obtaining the colour are not so easy to manage as when glyoxylic acid is used. In the latter case it may be that the amount of formaldehyde liberated by the acid is never in sufficient excess to interfere with the colour reaction, or else that the nascent formaldehyde so produced is extremely reactive in the formation of the colour.

Glyoxal and *glycollic aldehyde* also react with tryptophane. The derivatives thus obtained are at present being investigated.

A new type of parasitism in the Polychaeta. By F. A. Potts, M.A., Trinity Hall.

[*Read* 27 November 1911.]

The Syllids are a numerous and ubiquitous family of marine Polychaet worms, all of small size but varying considerably in their structure and habits. They are however alike in possessing a constant type of pharynx which can be protruded for the purpose of obtaining food and which is used in several forms at least as a weapon of attack upon other animals.

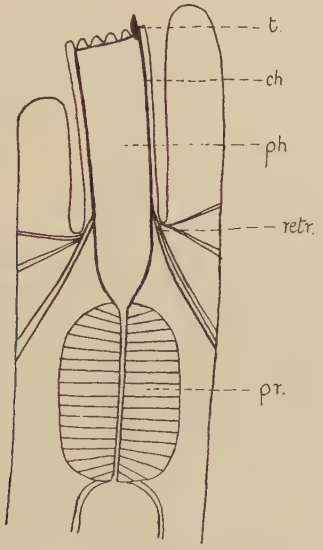


Fig. 1.

Diagram of anterior part of gut of typical Syllid with pharynx protruded. Lateral view. Lettering in text.

The structure of the anterior part of the gut (fig. 1) is very characteristic and may be briefly described as follows. Anteriorly there is the protrusible *pharynx* (*ph.*) contained during retraction within a definite *pharynx-sheath* (*ph. sh.*) and with a cuticular lining (*ch.*) of variable thickness. To this succeeds the barrel-shaped *proventriculus* (*pr.*) with thick walls of radiating muscle-fibres and a very narrow lumen. By the suctorial action of this latter organ food is drawn into the alimentary canal.

In the pharynx the chitinous lining may be locally thickened to form teeth which occur either singly (*t*) or arranged in a semicircle or complete circle. This armature is undoubtedly of great importance to the worm in feeding, and the most detailed observations as to its use we owe to Eisig*. Individuals of *Syllis* (*Haplosyllis*) *spongicola* were kept in aquaria into which various annelids of much greater size were introduced. All these were invariably assaulted and severely wounded. Even more savage is the behaviour of these worms with those of their own kind and their conflicts reminded Eisig of nothing so much as a dog-fight. By the cutting action of the single tooth or stylet deep wounds are made in the body of the enemy and portions of the flesh torn away which are crammed into the cavity of the pharynx.

Treadwell† has recently described the occurrence of two individuals of another species of the same genus (*Syllis* (*Haplosyllis*) *cephalata*), firmly fastened to the body of a large Eunicid Polychaet. In each case the Syllid was attached to a cirrus of the parapodium which had been swallowed and occupied most of the pharyngeal cavity. Treadwell claimed that the cirrus showed signs of digestion and that *Haplosyllis* might here be considered as an ectoparasite.

In the collections made by Mr Cyril Crossland in 1902 at Zanzibar, there is a Polychaet in which the ectoparasitic habit is undoubtedly normal and attachment to the host permanent throughout adult life. It can be definitely placed in the family Syllidae and I propose the new generic name *Parasitosyllis*. Individuals were found living on both Polychaet and Nemertine worms, fixed by the permanently protracted pharynx which is inserted in the body wall of the host and so intimately intergrown with its tissues that it was impossible to detach the parasites from their prey (save in the case of the soft bodied Nemertine) without breaking off the pharynx from the rest of the body. The worm is about 5 mm. long and several individuals may be found on a single host.

The pharynx (fig. 2, *ph.*) projects from the pharynx-sheath (*ph. sh.*) and rather resembles an elongated vase with a short stem, the rim of which is embedded in the body of the host while the stem, a narrow tube, communicates posteriorly with the proventriculus (*pr.*). Except in this posterior region the walls of the pharynx are enormously thickened and composed of at least four layers of chitin, without, as far as I am able to observe, any

* Eisig, *Fauna und Flora des Golfes von Neapel*, T. XXVIII.; *Ichthyotomus*, pp. 179—181. For similar observations on *Eusyllis*, see Malaquin, *Recherches sur les Syllidiens*, 1893, p. 246.

† Treadwell, *Haplosyllis cephalata* as an ectoparasite. *Bull. Amer. Mus. Nat. Hist.* Vol. XXVI. pp. 359—360.

cellular investment or lining. Anteriorly these chitinous layers run far into the host, bending round at right angles as they enter the body so as to extend between the skin and the musculature, becoming thinner and thinner as they penetrate so that it is soon extremely difficult to distinguish between the tissues of parasite and host. The lumen of the pharynx is narrow anteriorly and crammed with the tissues of the host: posteriorly it is even more restricted by the presence of a thick cushion of muscle (*mu.*)

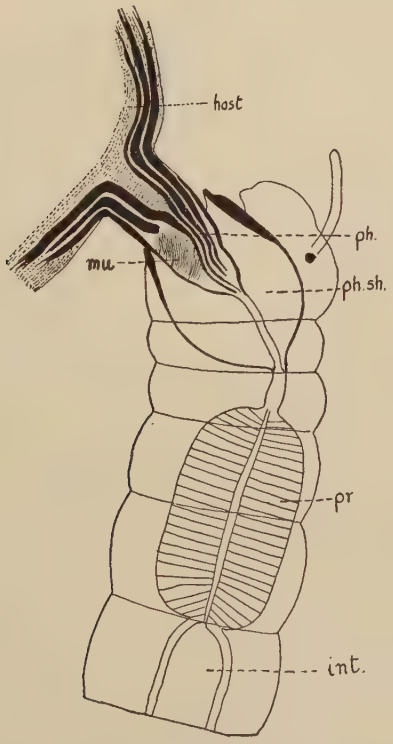


Fig. 2.

Diagram of anterior part of *Parasitosyllis* fixed to host. Lateral view. The dotted portion represents the body of the host, the dark black lines the chitinous layers of the pharynx which penetrate it.

which considerably obscures the relation of the parts. It is however possible to make out a narrow duct apparently communicating with the cavity of the proventriculus, which would serve for the passage of fluids absorbed from the host.

The pharynx is partly contained in a deep cup-shaped cavity, the pharynx sheath, the lips of which approximate anteriorly to

form a circular aperture. It may perhaps be suggested that at one stage of the life history of *Parasitosyllis*, before the extraordinary development of the pharynx has taken place, this aperture may function as a suctorial mouth and effect the first attachment of parasite to host. If at this period the pharynx was retractile and provided with stylets with which to cut a way into the body of the host, all traces of such a condition are now lost in the specimens here described and it must be left to future investigations to decide the methods of fixation.

The proventriculus is of the form only found in the Syllids and Hesionids among Polychaets. A testimony is given to the effective nature of its pumping action by the discovery that, in the only complete specimen, a parapodium of the host had been sucked into the pharyngeal cavity with such force that its setae were driven right into the chitinous walls of the pharynx.

With regard to the structure of the rest of the body little need be said here*. The head is provided with appendages of normal development and a pair of eyes. The parapodia are provided with dorsal and ventral cirri and a few simple setae. The intestine is a simple tube without coeca but thrown into a small loop posteriorly. The permanent fixation of the parasite is however responsible for the great reduction of the muscles of the body wall and possibly too for the fact that the setae hardly emerge from the parapodia.

In 1906, Eisig published an exhaustive memoir on a new genus of Polychaeta, *Ichthyotomus*, which is also an ectoparasite attached to its host by the pharynx. In the details of structure and habits it differs rather widely from *Parasitosyllis*. Eisig concluded that his discovery was nearly related to the Syllids but the likeness is obscured by changes consequent on parasitism. The animal is provided with a suctorial mouth (*Saugmund*) by which it first fixes on the skin of the eel which serves as host. The pharynx is then protruded and by means of the two stylets, like a pair of scissors in arrangement and form, a way is cut to the blood capillaries in the skin of the host. The stylets remain so firmly embedded in the tissues that it is only possible for the parasite to change its position as the result of very vigorous muscular action. The death of many individuals was in fact observed after unsuccessful efforts to free themselves but others were able to leave one host and reattach themselves to another.

Some clue to the derivation of the peculiar stylets of *Ichthyotomus* is furnished by the study of the form *Gnathosyllis diplodonta* which is the only Syllid known with paired stylets. The pharynx

* A full diagnosis will shortly be published in the *Transactions of the Linnean Society* in the course of a paper on "The Polychaeta of the Indian Ocean, Pt III, The *Syllidae*."

of Eisig's parasite is of the type seen in the larva of the Syllidae but the head appendages have become rudimentary owing to the close attachment of the anterior end of the parasite to the host. It is for these and other reasons that Eisig has created a separate family, the Ichthyotomidae.

Ichthyotomus exhibits further modification due to its life as a blood-sucking ectoparasite. A considerable development of "salivary" glands has taken place, and these almost certainly secrete a ferment preventing the coagulation of blood swallowed, as in the case of the medicinal leech and ticks. There is, too, a considerable expansion of the alimentary canal to contain as great a volume of blood as possible. In each segment of the body a pair of gut coeca are developed which fill up the entire body cavity and even extend into the parapodia and hollow dorsal cirri. In comparing, then, *Ichthyotomus* and *Parasitosyllis* we find that though in both the pharynx is highly modified it is in very different ways. The latter, too, subsisting possibly on the coelomic fluid of the host and not apparently on its blood shows, in the rest of its alimentary system, a much simpler organisation than *Ichthyotomus*.

Cytological Observations on Crossfertilised Echinoderm Eggs. By L. Doncaster, M.A., King's College, and J. Gray, King's College.

[*Read* 27 November 1911.]

In the *Journal of the Marine Biological Society*, Vol. ix. 1911, p. 121, Shearer, De Morgan and Fuchs have described observations on hybrid larvae obtained from reciprocal crosses between the three species of *Echinus*, *E. acutus*, *E. esculentus* and *E. miliaris*. Their most important result was that in reciprocal crosses the larvae in certain characters always resembled those of the maternal species. They have handed over to us for examination eggs in the early stages of segmentation from the cultures from which their larvae were reared, and the following is a preliminary account of the results of our work.

The crosses on which we have obtained the clearest results are those between the nearly related species *acutus* and *esculentus*. Careful counts of the chromosomes in these species have convinced us that the chromosome number in each species is 38; in each there is considerable diversity of form and size among the chromosomes, so that certain individual chromosomes can constantly be recognised, but we have not found any differences between the two species which are definite enough to be regarded as specific. In the cross *esculentus* ♀ × *acutus* ♂ the mitotic figures of the segmenting egg are perfectly normal, and do not differ recognisably from those of the pure species. In the converse cross *acutus* ♀ × *esculentus* ♂, however, a striking abnormality is constantly present in all the eggs examined. Until immediately after the dissolution of the nuclear membrane in the first segmentation division the behaviour is normal, and 38 normal chromosomes can be counted. As the spindle is formed, the chromosomes become scattered upon it irregularly, and gradually become collected in the equatorial plate. During this process it is seen that a considerable though variable number of them are either swollen up, or more commonly bear vesicles attached to their ends or sides. The staining of the vesicles is always less intense than that of the chromosomes, and is progressively fainter, the more the vesicle is developed, so giving the impression that the chromosome has swollen at one point, and that the chromatin is thus more thinly diffused in the wall of the vesicle than in the normal part of the chromosome. In the equatorial plate stage the vesicles may either remain attached to the chromosomes which produced them, or become separated from them; those which become separated tend to take up positions round the edge

of the equatorial plate, sometimes outside the spindle. The normal chromosomes, and those of which the normal shape has not become much altered by vesicle-production, then split longitudinally in the ordinary way, and begin to travel to the poles. It may sometimes be seen that a chromosome with a vesicle attached has split, and the vesicle, remaining attached to one half, is being carried with it towards the pole. It is possible that a few chromosomes, the greater part of which has become swollen into a vesicle, do not divide, but are carried entire to one or other pole. The vesicles which have become separated from their parent chromosomes appear to differ in their fate according to their position. If they lie among the chromosomes inside the spindle, they are carried with them to one or other pole and become included in the daughter nuclei. If, however, they are left on the edge of the spindle, as commonly happens with the larger vesicles, they remain outside the mitotic figure in the cytoplasm, and are not included in the nuclei of the daughter cells. In this case they usually contract and become small evenly stained spheres, not easily distinguishable from the larger yolk-granules, but usually recognisable after the cell-division is completed, lying in the cytoplasm near the boundary between the two cells.

In the second segmentation division, a similar process takes place, but is usually rather less pronounced; the vesicles are on the whole smaller, and we doubt whether complete chromosomes ever become vesicular.

In both divisions the number of vesicles varies, ranging in anaphase stages from one to half a dozen or perhaps more; in the equatorial plate as many as a dozen chromosomes may be seen to bear small vesicles, but some of these are probably either reabsorbed, or if they are thrown off, become too small to be recognisable in anaphase. The vesicles are in appearance rather like those normally formed in late anaphase by typical chromosomes, which at that stage swell up into vesicles as they unite to form the daughter nucleus. Like the latter, they have the chromatin aggregated in minute masses round the periphery, but they differ in staining rather more evenly, especially in sublimate preparations, so that the vesicles formed in the prophase can be distinguished from those normally produced in late anaphase even when they are mixed together in the cluster about the pole of the spindle. After the daughter nuclei are formed, the vesicles which have become included are no longer recognisable.

That a number of chromosomes which produce vesicles afterwards behave normally is shown not only by observations on the stage when they are splitting, but also by counts of the chromosome number in anaphase. The normal number should be 38, the actual numbers counted range in first divisions from about

31 or 32 to 37, in second divisions from 32 to 38, the two ends of a single spindle not always giving the same result. There is, however, no regular relation between the chromosome number and the number of vesicles; it is clear that a chromosome may throw off a vesicle and then divide normally. On the other hand the almost constantly smaller number of chromosomes in anaphases of these eggs indicates either that a small number of chromosomes are completely used up in forming vesicles, or that they are prevented from dividing normally. The anaphase groups are less regular than in normal eggs, and it is not always possible to say with certainty whether they include an undivided chromosome or not.

Our observations on the cross with *miliaris* are less complete and satisfactory than those with the *acutus-esculentus* crosses. The material included only the combination *acutus* ♀ × *miliaris* ♂, and different batches of eggs gave somewhat discordant results. The determination of the chromosome number in pure *miliaris* eggs is less certain than in the other species; in some eggs we have found 36, in others not more than 34 are recognisable. The spindles of *miliaris* are narrower, and the chromosomes more crowded, than in *esculentus* and *acutus*, and a remarkable point about the *acutus* ♀ × *miliaris* ♂ eggs is that the spindles have the *miliaris* form, or are often still narrower, although the cytoplasm in which they are formed is that of *acutus*. The chromosomes of *miliaris* are more uniform than those of the other species, so that in the hybrids certain chromosomes can be recognised as of maternal origin. The narrowness of the spindles and consequent crowding of the chromosomes, usually, however, makes the identification difficult.

In one lot of *acutus* eggs fertilised by *miliaris* sperm the segmentation mitoses are mostly quite regular, with no vesicle formation. In only an occasional egg can one or more small vesicles be seen. In other lots of hybrid eggs vesicles are frequent, occurring in nearly every spindle; they are smaller than those in the *acutus* ♀ × *esculentus* ♂ eggs, and it is probable that whole chromosomes never become vesicular. In one batch of eggs all stages are represented from the first division to about the 16- or 32-cell stage, and in the early divisions vesicles are constantly present, while in the later stages they are absent. Unless the more backward eggs are abnormal (and it should be noted that in this batch they frequently show multipolar spindles and division of nuclei without segmentation of the cytoplasm), this indicates that the vesicle formation takes place only in the earlier divisions, and that the chromosomes recover their normal behaviour later. The chromosome number is difficult to determine with accuracy; in the batch in which vesicles are

rare we find from 32 to 35 or 36; in those in which vesicles are more frequent the number appears to be rather lower, but we cannot place very great confidence in the accuracy of our counts in these cases. The chromosomes show a tendency to aggregate into small clumps, and it is difficult to determine the number in such a group, or to decide whether any chromosomes have passed over undivided. The fact that the number counted is constantly less than the normal expectation, and the presence of chromosomes which either by their thickness, or from their appearance of being partially split, suggest that they have failed to divide, makes us inclined to believe that in this case some few chromosomes may pass over undivided in the first division.

We prefer to leave any discussion of the theoretical bearings of our work, and of comparison with the results obtained by others, until the publication of the fuller paper. One of us is engaged in working at the physical conditions associated with the vesicle formation.

On the double-six which admits a group of 120 *collineations into itself.* By W. Burnside, M.A., F.R.S.

[*Received* 4 December 1911.]

It has not, I believe, been hitherto recognised that the configuration of the double-six presents itself in one of the fundamental configurations of the projective geometry of space.

A projective transformation of space is uniquely determinate when the new positions A', B', C', D', E', into which five arbitrary points A, B, C, D, E are changed by it, are given; it being understood that no three of either of these sets of five points lie in a line and no four in a plane. Five points may be permuted among themselves in 120 ways. There thus arises a group of 120 collineations for which the set of five points, as a whole, is invariant. There is a one-to-one correspondence between the collineations of the group and the permutations of the symbols of the five points. The permutation group of five symbols, *i.e.* the symmetric group of degree 5, has six cyclical sub-groups of order 5. Each of the corresponding cyclical collineation groups has two fixed straight lines; and the set of six line pairs that so arise, do in fact constitute a double-six. This is the double-six that admits a group of 120 collineations into itself.

Notation. A, B, C, D, E are five points, no three of which lie in a line and no four in a plane. The collineation which corresponds to a given permutation of the points will be denoted by the symbol of the permutation; thus $(AB)(CDE)$ denotes the collineation which changes A into B, B into A, C into D, D into E, E into C.

Let M, N be the points in which a line through A meets the lines BC and DE, and let P be the harmonic conjugate of A with respect to M and N. Similarly let Q and R be the harmonic conjugates of A with respect to the pairs of points in which lines through A meet BD, CE and BE, CD respectively. Then any collineation of the group which leaves A unchanged permutes P, Q and R, and leaves the plane PQR unchanged. This plane will be called a, and the planes similarly constructed from the other points, b, c, d and e. Any collineation of the group gives the same permutations of A, B, C, D, E and of a, b, c, d, e. Thus the collineation $(AB)(CDE)$ is equally well denoted by the symbol $(ab)(cde)$. For the line through A meeting BC and DE the symbol $A.BC.DE$ will be used. The line of intersection of a and b will be denoted by ab; and the line joining the points in

which bc and de meet a by $a.bc.de$. The point of intersection of a, b and c will be called abc. The collineation $(BE)(CD)$ leaves three points, and therefore every point on the line $A.BE.CD$ unchanged. Similarly it leaves every plane through $a.be.cd$ unchanged. Further the same collineation leaves the three planes ABE, ACD and that through $A.BE.CD$ and abe unchanged. Hence it leaves every plane through $A.BE.CD$, and therefore every point of $a.be.cd$ unchanged.

The two lines $A.BE.CD$ and $a.be.cd$ are non-intersectors. For if they met in I every line through I would be unaltered by $(BE)(CD)$. Hence BE and CD would intersect in I, and B, C, D, E would lie in a plane, contrary to supposition.

Let λ_1, λ_2 be two lines intersecting $A.BE.CD$, $a.be.cd$, $D.AB.CE$ and $d.ab.ce$. They are unaltered by the collineations $(BE)(CD)$ and $(AB)(CE)$. Hence they are unaltered by the collineation that arises on carrying these out in succession, viz. $(ABCDE)$, and by any repetition of the latter. Now

$$(ABCDE)^2 = (BE)(CD).(AC)(DE),$$
$$(ABCDE)^3 = (BE)(CD).(AD)(BC),$$
$$(ABCDE)^4 = (BE)(CD).(AE)(BD).$$

Hence λ_1 and λ_2 are unchanged by $(AC)(DE)$, $(AD)(BC)$ and $(AE)(BD)$. They therefore meet $B.AC.DE$, $b.ac.de$, $C.AE.BD$, $c.ae.bd$, $E.AD.BC$ and $e.ad.bc$.

If a third line μ met $A.BE.CD$, $a.be.cd$, $D.AB.CE$ and $d.ab.ce$, it would also necessarily meet $B.AC.DE$, $b.ac.de$, $C.AE.BD$, $c.ae.bd$, $E.AD.BC$ and $e.ad.bc$. Then if P is the point in which μ meets $A.BE.CD$, there is a unique projective transformation which leaves every point of λ_1 and λ_2 unchanged and changes P into A. This transformation changes μ into a line through A which meets $B.AC.DE$, $C.AE.BD$, $D.AB.CE$ and $E.AD.BC$. The existence of such a line is obviously inconsistent with the condition that no four of the points A, B, C, D, E lie in a plane.

Hence λ_1, λ_2 are the only lines which meet the five pairs and the only lines unchanged by $(ABCDE)$. Now the collineation $(BCED)$ leaves $A.BE.CD$ and $a.be.cd$ unchanged and permutes the other four pairs. It must therefore permute λ_1 and λ_2.

Denote by λ_{1i}, λ_{2i} $(i = 1, 2, \ldots, 6)$ the six pairs of lines (each pair clearly non-intersectors) which are unchanged by the six cyclical sub-groups of collineations of order 5: and suppose the suffixes so chosen that the sets λ_{1i} $(i = 1, 2, \ldots, 6)$ and λ_{2i} $(i = 1, 2, \ldots, 6)$ are separately permuted among themselves by collineations which correspond to even permutations, the two sets being interchanged by any collineation corresponding to an odd permutation.

If λ_{1i}, λ_{2i} are the fixed lines for $(ABCDE)$ and λ_{1j}, λ_{2j} for $(ABDCE)$, then since

$$(CD)(ABCDE)(CD) = (ABDCE),$$

(CD) changes λ_{1i} into λ_{2j} and λ_{1j} into λ_{2i}. Now (CD) leaves every point of $A.BE.CD$ unchanged, and changes λ_{1i}, which meets $A.BE.CD$ into λ_{2j}. Hence λ_{1i}, λ_{2j} and $A.BE.CD$ meet in a point. Also (CD) leaves every plane passing through $a.be.cd$ unchanged, and changes λ_{1i}, which meets $a.be.cd$ into λ_{2j}. Hence λ_{1i}, λ_{2j} and $a.be.cd$ lie in a plane.

Similarly λ_{2i}, λ_{1j} and $A.BE.CD$ meet in a point and λ_{2i}, λ_{1j}, $a.be.cd$ lie in a plane.

Since λ_{1i}, λ_{2i} and λ_{1j}, λ_{2j} may be any two pairs out of the six pairs of intersectors, this completes the proof that the six pairs form a double-six; while it is clearly invariant for the group of collineations considered.

Conversely, if a double-six is unchanged by a group of 120 collineations, its six pairs of non-intersectors must be permuted by every collineation. The only permutation groups of six symbols of order 120 are a transitive group, and an intransitive group leaving one symbol unaltered, each simply isomorphic with the symmetric group of degree 5. There is a group of collineations of order 120 which leaves a pair of non-intersectors unchanged, but it does not permute sets of five points on the two lines. Hence the first is the only possibility. Now there is only one group of collineations of space, simply isomorphic with the symmetric group of degree 5, which has not an invariant line-pair; and it is that already considered. Hence a double-six which is invariant for a group of 120 collineations must arise as above, and all such double-sixes are projectively equivalent.

A Magnetic Examination of the Function of the Water Molecule in certain Dilute Solutions. By A. E. Oxley, M.Sc., B.A., Trinity College.

[*Received* 13 December 1911.]

Introduction. According to the modern hydrate theory of solutions, as developed by H. C. Jones from considerations based on conductivity and lowering of the freezing-point determinations, the total amount of water associated with the solute increases with the concentration, and further the number of water molecules associated with one molecule of the solute increases with the dilution. This has been shown to be true for a large number of salts*.

Now paramagnetism depends upon the facility of orientation of the molecular axes and this is opposed on the one hand by the inertia of the molecular system, and on the other hand by the mechanical impacts with other systems. Consider the case of the solution of a salt of a ferromagnetic element in water. If the solution be concentrated the hydration will be relatively small and we might expect that the susceptibility of such a solution would be proportional to the number of salt molecules it contains, *i.e.* to the amount of ferromagnetic element present. But at considerable dilution the hydration becomes large and each of the comparatively few salt molecules in the solution has a considerably increased inertia. These loaded molecules might therefore be more reluctant to fall into alignment with the direction of the magnetic field and the molecular axes would not swing round nearly so far before collisions re-distributed the axes. Consequently we might expect there would be an abnormal decrease in the paramagnetic susceptibility of the solution.

The susceptibilities of a series of dilute solutions of several salts have been determined in order to ascertain if such a reduction in paramagnetism takes place.

Method. The du Bois electromagnet used in a previous research† was provided with conical pole pieces and a U-tube method was adopted to measure the susceptibilities as the torsion method employed in that research proved to be very sensitive to vibration.

* *Vide* H. C. Jones, "Hydrates in aqueous solutions."

† *Proc. Camb. Phil. Soc.* Vol. xvi. Pt 1, p. 102.

By means of stops at S', S'' the U-tube could be replaced in almost exactly the same position and usually no further focussing of the microscope M was needed. An approximate value of the displacement was found in each case and the level of the meniscus altered by the screw S so that when the field was excited the meniscus moved to a definite division of the eye-piece scale. On squeezing the tube R the solution could be made to rise and fall in the field of view and thus smooth motion of the meniscus was ensured by keeping the wall of the tube wet.

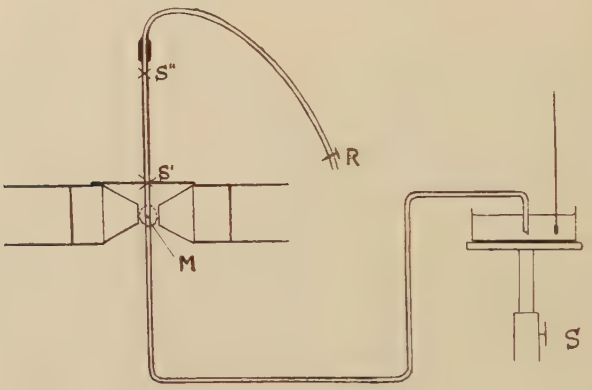


Fig. 1.

The susceptibility per unit volume (χ) of a solution is given by

$$\chi = \chi_a - \frac{\rho_1 d_1}{\rho_2 d_2}(\chi_a - \chi_w)^*$$

where χ_a is the susceptibility of air $= 0{\cdot}25 \times 10^{-7}$ per unit volume,
χ_w „ „ „ water $= -7{\cdot}5 \times 10^{-7}$ per unit volume,
ρ_1 is the density of the solution,
ρ_2 „ „ water,
d_1 „ displacement of the solution meniscus,
d_2 „ „ „ water meniscus for the same field intensity.

Experiments. The original solutions were made by dissolving the pure salts in carefully distilled water and from these solutions of one half, one quarter, etc. the original concentrations were made by measurements taken in a burette tube. Usually four or five dilutions were made but for any number of such dilutions the maximum error cannot amount to more than four times the

* *Loc. cit.* p. 106.

error of taking a single burette reading, and as 60 c.c. of each solution were taken at once, the error arising from dilutions is negligibly small. Each original solution was subjected to a quantitative chemical analysis and occasionally a solution of higher dilution was analysed as a check on the above.

The amount of salt per c.c. was estimated volumetrically in the case of the nickel salts, using standard solutions of potassium chloride and potassium cyanide. A gravimetric method was used for estimating the cobalt solutions, the cobalt being precipitated with potassium nitrite in the presence of acetic acid.

In the following tables Δ is the mean displacement of the meniscus for the magnetic field corresponding to the current stated, C is the concentration of the solution in grammes of salt per c.c., ρ is the density of the solution, and χ the susceptibility.

TABLE I. *Nickel sulphate (A).*

Current 3·61 amps., pressure 753 mm., temperature 17·1° C.

Solution	Δ	C	ρ	$-\chi \cdot 10^7$
A	22·56	·0111	1·012	4·21
$\frac{1}{2}A$	30·96	·0055	1·006	5·80
$\frac{1}{4}A$	35·54	·0027	1·003	6·70
$\frac{1}{8}A$	37·65	·0014	1·002	7·11
$\frac{1}{16}A$	38·80	·0007	1·001	7·33
Water	39·65	—	1·000	7·50

TABLE II. *Nickel nitrate (B).*

Current 3·61 amps., pressure 755 mm., temperature 17·1° C.

Solution	Δ	C	ρ	$-\chi \cdot 10^7$
B	17·76	·0156	1·014	3·26
$\frac{1}{2}B$	29·02	·0078	1·007	5·42
$\frac{1}{4}B$	34·44	·0039	1·003	6·48
$\frac{1}{8}B$	36·96	·0019	1·002	6·97
$\frac{1}{16}B$	38·45	·0010	1·001	7·27
Water	39·65	—	1·000	7·50

TABLE III. *Nickel chloride (C).*

Current 3·17 amps., pressure 763 mm., temperature 17·2° C.

Solution	Δ	C	ρ	$-\chi.10^7$
C	−11·36	·0274	1·024	—
$\frac{1}{2}C$	+11·35	·0137	1·013	2·52
$\frac{1}{4}C$	21·45	·0069	1·006	4·95
$\frac{1}{8}C$	26·73	·0034	1·003	6·23
$\frac{1}{16}C$	29·29	·0017	1·001	6·86
Water	32·00	—	1·000	7·50

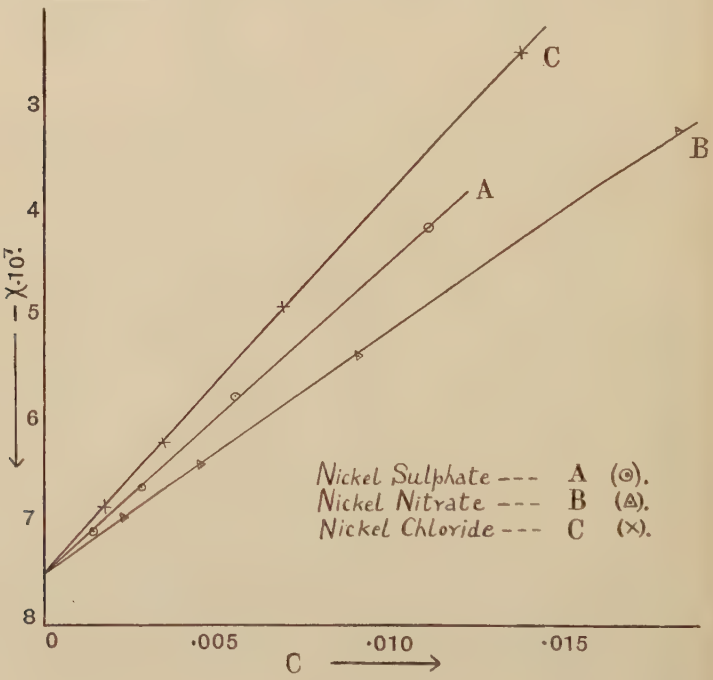


Fig. 2.

From the curves of fig. 2 it is seen that the relation between concentration and susceptibility is linear, and if M be the mass of nickel per c.c. of solution, then the susceptibility of the solution is given by

$$10^7 \chi = 817M - 7{\cdot}50,$$

a relation similar to that found by Townsend* for iron salts.

* *Phil. Trans.* A. 1896, p. 533.

TABLE IV. *Cobalt chloride (D).*

Current 3·18 amps., pressure 758 mm., temperature 17·4° C.

Solution	Δ	C	ρ	$-\chi.10^7$
D	11·55	·00622	1·0058	2·51
$\frac{3}{4}D$	16·50	·00465	1·0050	3·70
$\frac{1}{2}D$	21·91	·00311	1·0029	5·00
$\frac{1}{3}D$	25·71	·00207	1·0019	5·90
$\frac{1}{4}D$	27·40	·00155	1·0015	6·30
$\frac{1}{8}D$	30·00	·00078	1·0007	6·93
$\frac{1}{16}D$	31·24	·00039	1·0004	7·22
Water	32·40	—	0·9988	7·50

TABLE V. *Cobalt chloride solution (D'), diluted with hydrochloric acid.*

Current 3·18 amps., pressure 760 mm., temperature 16·8° C.

Solution	Δ	C	ρ	$-\chi.10^7$
D'	9·61	·00648	1·0062	2·06
$\frac{3}{4}D'$	15·51	·00486	1·0432	3·62
$\frac{1}{2}D'$	20·80	·00324	1·0803	5·12
$\frac{1}{4}D'$	26·20	·00162	1·1173	6·75
$\frac{1}{8}D'$	28·80	·00081	1·1358	7·55
$\frac{1}{16}D'$	30·00	·00040	1·1450	7·97
HCl	31·10	—	1·1540	8·33
Water	32·40	—	0·9988	7·50

The values of χ and C are plotted in fig. 3, but in the D curve the diamagnetic susceptibility of each solution has been increased by unity in order to separate the curves. A solution of hydrochloric acid and water of density 1·129 had a susceptibility $-7{\cdot}90 \times 10^{-7}$, and so the relation between concentration and susceptibility for hydrochloric acid and water is linear.

From the curves it is clear that the susceptibility of an aqueous solution of a salt is accurately proportional to the concentration; and the hydrates, whose existence is confirmed by conductivity and lowering of the freezing-point determinations and absorption effects, must be of such a nature as to allow the magnetic properties of the solution to be unaltered as their complexity

increases with dilution. If we suppose the water molecules to be condensed round the salt molecule as nucleus, and further assume sufficient instability on the part of the system so produced

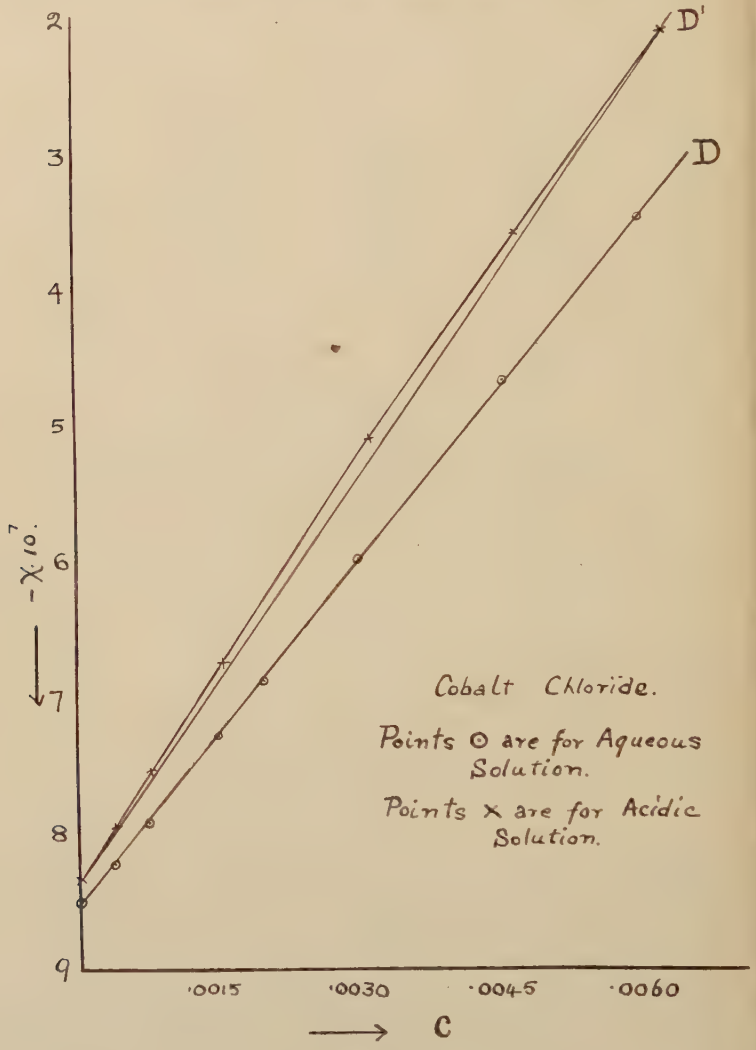


Fig. 3.

that on the application of a magnetic field the salt molecule alone shall orientate, then the effect of complex hydration will not enter at all. On the other hand the effects observed by Jones will still be valid since they depend upon the size of the system

and not upon its structure. That these hydrates are of such an unstable nature is confirmed by the ease with which they break up on a slight increase in temperature.

But it is not essential that the nucleus should be a simple salt molecule. It may be a salt molecule together with several molecules of water of crystallization, united to the salt molecule chemically, and distinct from the hyper-hydrates considered above. This is probably the case with all salts and determines the quantity of the water associated with the salt on crystallization. If by means of some dehydrating agent we could compel a portion of the chemically combined water to leave the salt we should expect a rise in paramagnetic susceptibility. This appears to be the case with the acidic solution of cobalt chloride in Table V. The solution *D′* is one of cobalt chloride in water and the succeeding solutions were made by dilutions with hydrochloric acid. There is an appreciable curvature of the susceptibility curve corresponding to a gradual change in colour from the pink to the blue solution. The fact that the blue solution sometimes deposits crystals of anhydrous cobalt chloride is evidence that some of the salt molecules in the blue solution are dehydrated.

Summary.

The complex hydrates, whose existence is indicated by conductivity and lowering of the freezing-point determinations, cannot be detected by their effect on the magnetic property of the solute. This is what may be expected if the hydrates themselves are unstable enough. The nucleal salt molecule or ion rotates independently of the condensed shell of water molecules on the application of the magnetic field. In the case of cobalt chloride there appears to be a definite chemical hydrate in solution part or all of whose combined water can be removed by a strongly dehydrating agent. The solution so dehydrated has a maximum increase in paramagnetic susceptibility amounting to three per cent.

In conclusion I wish to thank Prof. Sir J. J. Thomson for the great interest he has taken in this work.

A Note on short Wave Lengths in the Mercury Arc Spectrum. By A. Ll. Hughes, M.Sc., B.A., Research Scholar of Emmanuel College. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 15 December 1911.]

In experiments on the photo-electric effect, it is often of importance to know the shortest wave length in the spectrum of the light used in the experiments. The most convenient source of ultra-violet light is the mercury arc in quartz glass. A photograph of the spectrum of the light from such a mercury arc showed that the shortest wave length was apparently about λ2300. However, it was found that the unresolved light from this arc produced electrons of much greater velocities than those produced by the isolated group of wave lengths between λ2300 and λ2400. It was therefore suspected that there were shorter wave lengths in the spectrum than were indicated on the plates. A number of photographs were taken with exposures varying from five to twenty minutes. (An exposure of two or three seconds was sufficient to show all the lines up to λ2300.) The plates were all more or less fogged, but on some of them, certain faint lines were observed in the extreme ultra-violet. These lines appeared on ten out of the eighteen plates that were exposed. In order to calculate the wave lengths of these lines, photographs of the spectrum of the Al spark were taken on the same plates. There are four well known lines in the ultra-violet spectrum of the Al spark, viz. λ1854, λ1862, λ1935 and λ1990. Taking these lines as standard, a quadratic formula connecting the wave lengths and the distance apart was used in calculating the new wave lengths in the Hg arc spectrum. The new wave lengths are given in the following table together with the wave lengths attributed to the last three by Stark * and by Steubing †.

The fact that λ1849 is the shortest wave length in the light from a mercury arc in quartz glass is shown in the following way. The maximum velocity of electrons emitted from a certain zinc surface was found to be 2·02 volts‡, when the unresolved light from the mercury lamp fell upon it. The light was then passed through a spectroscope and the maximum velocities corresponding to individual wave lengths were investigated. All wave lengths, except λ1849, gave smaller maximum velocities than the unresolved light. It appears therefore that λ1849 is the shortest

* *Ann. d. Phys.* xxi. 1906, p. 457.

† *Verh. d. Deutsch. Gesell.* 1909, p. 563.

‡ It is convenient to express the velocities of the electrons in terms of the potential difference which is necessary to reduce their velocities to zero.

wave length in the light emitted by the mercury lamp used in this experiment. The maximum velocity corresponding to λ1849 was 2·06 volts, a little higher than that corresponding to the unresolved light. This small difference is easily explained by the fact that it is difficult to avoid a slight scattering of the light from the illuminated plate to the surrounding electrode. The scattered light causes an emission of electrons to the plate, tending to reduce its potential. The effect is larger when all wave lengths in the ultra-violet are scattered than when only one wave length is scattered.

	Stark	Steubing
1849	—	—
*1909	—	—
1941·5	1941·77	1940
1972	1972·36	1971
2002	2002·24	2000

* Appeared only on three plates. Very faint.

A photo-electric investigation* of the spectrum of the mercury arc showed that it extended as far as λ1230 and that there was a gap between λ1780 and λ1450. (The mercury arc and the apparatus for indicating the wave length were in the same vacuum.) Taking these results in conjunction with the present experiment, it shows that the absorption of quartz glass begins somewhere between λ1780 and λ1849; to know exactly where the absorption starts would require a knowledge of the mercury arc spectrum between these wave lengths. A detailed examination of the spectrum in this region would probably require Schumann plates. The plates used in this work, Wratten and Wainwrights' Panchromatic and Verichrome, were almost insensitive in the extreme ultra-violet. The photo-electric effect, however, increases very rapidly with decreasing wave length and appears to show that λ1849 is the shortest appreciable wave length emitted by the mercury arc in quartz glass.

The spectrograph used in this investigation was obtained by means of a Government Grant from the Royal Society.

* *Phil. Mag.* (6) xx. 1911, p. 393.

*The Coagulation of Colloidal Copper. Rate of Coagulation**. By H. H. Paine, M.A., B.Sc., late Scholar and Coutts Trotter Student, Trinity College, Cambridge.

[*Received* 22 January 1912.]

§ 1. *Introductory.*

The addition of an electrolyte to a clear colloidal solution results, generally, in the coagulation of that solution. The liquid becomes opalescent, owing to the increase in size of the particles; individual particles gradually become visible, and ultimately settle to the bottom of the vessel, leaving the liquid above quite clear.

The study of coagulation in the above sense has usually taken the form of a determination of the minimum concentration of the electrolyte required to bring about, within a certain time, some particular change in the appearance of the solution (such as opalescence, or, better, the complete separation of the colloid as a precipitate). It has long been recognised, however, that concentrations of the electrolyte insufficient for bringing about this change in a short time—a few minutes, say—may yet be sufficient for the purpose if the liquid be allowed to stand for several hours, or perhaps days.

Again, Duclaux and others have advanced the idea that coagulation is really a "time process," that during it, the amount of substance in the colloidal state decreases gradually.

That the process of coagulation is a gradual one can often be seen quite easily; but in order to trace it quantitatively, it is necessary to be able to distinguish clearly the coagulated material from the uncoagulated. Here a theoretical difficulty seems to present itself. If coagulation consists in the continuous coalescence of colloidal particles to form larger and larger masses, at what stage in this process are we to say that the masses in question represent the coagulated portions of the colloid? There seems to be exactly the same sort of continuity in this case as exists between the colloidal state and the state of coarse suspension. In practice, however, the difficulty is overcome by regarding that part of the colloidal substance which is easily separated from the clear solution—that is to say, the *precipitated* part—as the coagulated portion. The amount of the precipitate formed will then give us a measure of the *extent of coagulation.*

* Portions of this paper, on the Rate of Coagulation, were communicated to the Chemical Section, British Association, Portsmouth, 1911.

The properties of copper hydrosol are such as enable us to vestigate the phenomena associated with these ideas. When is hydrosol is coagulated, the precipitate can be made to settle ite rapidly, so that the clear solution can be drawn off; further- ore, the estimation of the copper content of these solutions can sily be made.

§ 2. *The Preparation of Colloidal Copper.*

The copper solutions examined were prepared by Bredig's ethod, namely, by means of an arc discharge under pure water tween terminals of the metal. The actual arrangement used as as follows. The electrodes consisted of very stout copper res. One of them was held fixed in a clamp, while the other as kept continuously rubbing lightly against it by means of an centric on the axle of a small motor. "Making" and "breaking" us occurred with high frequency, so that the discharge was pt up almost continuously. A potential difference of about ty volts was used for supplying the current. It was noticed at, though the solution of copper consisted of positively charged rticles, the whole of the metal came from the cathode (which as worn smooth). The anode presented quite a blistered appear- ce at the part where the discharge had taken place. The Jena sk in which the solution was prepared was placed in a bath, rough which a stream of cold water was made to pass.

In this way, reddish-brown solutions were obtained, which adually darkened on being allowed to stand—partly on account the settling down of some larger and lighter-coloured particles n off in the discharge, and perhaps, also, on account of some ange, chemical or other, in the colloid particles. The solutions ere never filtered, as so much of the colloid is thereby with- awn. After preparation, they were allowed to stand for a day two, so that any large particles, or suspended matter, might ttle. The clear liquid was then drawn off into another flask.

The concentration of these solutions, as thus obtained, mained practically constant for days. A very slow, but con- nuous, deposition of the colloidal substance was always noted, wever; but this was not sufficient to produce an appreciable ror in the results of the longest series of experiments carried t.

The water used for preparing the solutions had been redistilled a Jena glass apparatus (after the addition of small quantities of lphuric acid and potassium bichromate). Its conductivity was nerally about $1{\cdot}0 \times 10^{-6}$ reciprocal ohms per centimetre cube at ° C., and the conductivity of the solutions varied from 1×10^{-6} 3×10^{-6} in the same units.

§ 3. *The Action of Nitric and Sulphuric Acids.*

The effect of acids upon the copper colloidal solution wa determined. Nitric and sulphuric acids were chosen for ex periment—the one containing a monovalent anion, and the othe a divalent.

It was found that on the addition of nitric acid, no coagulatio was brought about. The solution of copper became graduall paler in colour as the amount of acid increased, until, at a certai point, the colour disappeared altogether. Throughout the whol process no trace of any cloudiness or coagulation could be detected Allowing solutions containing less acid than was required t destroy the colour to stand for twenty-four hours, gave no differen result.

Raising the temperature of the solution greatly increased th *rate* at which the nitric acid "dissolved" the copper, but th *extent* of the action was unaltered thereby.

That the acid was neutralised by the copper was made eviden by adding to the solution a drop of methyl orange. Until th copper was dissolved, the indicator did not suffer any change, bu a slight excess of the nitric acid caused the solution to becom pink.

When an amount of sulphuric acid was used, equivalent t that of the nitric acid which dissolved the copper, the result wa the same as before. Smaller quantities, however, dissolved pa of the colloid and coagulated the remainder.

Since we are dealing with a positive colloid, it is the anion the electrolyte which is effective in bringing about coagulatio In this action the divalent sulphate ion is much stronger than th monovalent nitrate ion. It so happens that the concentration the hydrogen ions required to dissolve the copper is smaller tha the concentration of the nitrate ions, but greater than that of th sulphate ions, required to produce coagulation.

If the colloid be first of all coagulated with a salt containing monovalent anion, the addition of nitric acid results in the re formation of the colloidal solution (a clear brown or yellow liqui and then in the disappearance of the colour of this solutio When the coagulation is brought about by a salt containing divalent anion, this intermediate stage does not occur; th solution of the precipitate to a colourless liquid takes pla directly.

The amount of nitric acid necessary for dissolving the collo is directly proportional to the amount of colloid present, an independent of the dilution. Exactly the same quantity of ac is required whether the colloid be still in solution or whether be precipitated first of all.

The simplest explanation of this reaction lies in the solution of the copper by an equivalent amount of acid to form cupric nitrate, which in such minute quantities gives a practically colourless solution. In order to test this hypothesis, the quantity of copper in 250 c.c. of the solution was determined by a gravimetric process. The colloid was precipitated by a few cubic centimetres of a dilute sodium sulphate solution, washed with distilled water, collected on a filter, and dried. It was finally ignited (with the filter paper) in a weighed crucible, after the addition of a couple of drops of concentrated nitric acid, and weighed as CuO.

The amount of Na_2SO_4 introduced into the colloidal solution was 0·0023 gram. Of this, the sodium ions formed may safely be regarded as having remained in the liquid, and having been separated from the precipitate*. The sulphate ions were in part absorbed; consequently some of the copper in the crucible was present as $CuSO_4$. Since this absorption only amounts to about one quarter of the quantity added†, the necessary correction is small (about 0·0004 gram), and any uncertainty as to its exact value is of little consequence.

This experiment gave 0·041 gram as the mass of copper present in 250 c.c. of the colloidal solution studied. A titration with nitric acid solution (standardised with sodium carbonate) gave the value 0·045 gram for the copper content of 250 c.c.—on the assumption that the copper is "dissolved" by an equivalent amount of acid, that is to say, one gram-atom of Cu by two gram-molecules of HNO_3. The agreement between these two values confirms the explanation given of the action of nitric acid—that colloidal copper is dissolved by its equivalent weight of acid.

The existence of this equivalence provides us with a very convenient method for estimating colloidal copper, viz. that of titrating with dilute nitric acid. The disappearance of the brown or yellow colour of the solution, or of the bulky particles of the precipitate—which takes place quite rapidly when the liquid is hot—forms an easy and accurate method of observing when the copper is dissolved. In all the colloid estimations made in the following experiments, this was the method adopted. Since there were only about 4 milligrams of copper in 25 c.c. of any of the original solutions used, a gravimetric method was out of the question, as being too inaccurate and too laborious for a long series of experiments.

Only neutral salts which did not undergo hydrolysis were used for producing coagulation, so that the titrations were not complicated by a superposed acidity or alkalinity. But there is another fact which requires consideration in this connection. In the

* Linder and Picton, *J. C. S. Trans.* LXVII. p. 66. † See later.

addition of salts to positive colloids, a certain number of hydroxyl ions are liberated, equivalent to the anions absorbed by the colloid*. As long as the particles from which these hydroxyl ions are liberated remain in the solution, the result is quite unaffected ; but when some of them are precipitated and removed from the liquid so as not to be titrated the ones that are left will have a larger number of these ions associated with them. This excess would go to the neutralisation of part of the acid used in titration. The calculation just given of the amount of sulphate ions absorbed shows at once that the error thus introduced is quite small (never more than 1 °/₀) and may safely be neglected in practice.

The question arises whether the result of the chemical equivalence between the copper and the nitric acid in the reaction here considered throws any light on the composition of the particles themselves. Nitric acid dissolves metallic copper according to the equation

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

With cupric oxide (or hydroxide) the equation would be simply

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

The results of the experimental analysis described above show that the proportion of Cu and HNO_3 involved in the solution of copper hydrosol satisfies the second equation but not the first, as though the particles consisted of the oxide or hydroxide of copper and not of the metal itself. However, the action of nitric acid on metallic copper as shown in the first equation may be complex; an atom of Cu may be dissolved by two molecules of HNO_3, the "nascent" hydrogen liberated afterwards reducing some of the excess of HNO_3. It may then be urged that with such finely divided material as we have in a colloidal solution, and with such small traces of nitric acid, this secondary reaction may not occur. But in this case we should expect an evolution of hydrogen, which, for every 25 c.c. of the solution (containing ·004 gram of copper), would amount to more than 1 c.c. in volume. The evolution of such an amount could not fail to be detected, whereas no trace of effervescence occurred. The evidence therefore seems to be entirely in favour of regarding the particles as consisting of cupric oxide or hydroxide. Metallic copper is certainly torn off in the discharge during the preparation of the solution, for large quantities of it collect on the bottom of the preparation flask, and show the ordinary reaction with nitric acid. It is probable, therefore, that the oxidation of the colloid particles is a subsequent effect, and may be partly responsible for the darkening of the solution observed after the preparation.

* Whitney and Ober, *J. Amer. C. S.* 1901, xxiii. p. 842.

§ 4. *The Coagulation of Colloidal Copper with Mono- and Di-valent Anions.*

When a solution of colloidal copper is coagulated by means of an electrolyte, the precipitated particles flock together on gently shaking and settle fairly rapidly. If the coagulation be complete the supernatant liquid will be colourless, while for intermediate stages it will have the brown or yellow colour of the substance still remaining in solution.

This flocking together of the coagulated particles, whereby rapid settling is brought about, was aided in one of two ways. In the *first* the liquid was heated till it was close on boiling and then placed to stand, while in the *second* it was gently stirred without having recourse to heating at all. The first we shall refer to as the "*hot*" method and the second as the "*cold*." Both these methods introduce complications which will have to be considered later. The general (qualitative) results are unaffected, however, and for the present it is with these only that we shall deal.

Rate of Coagulation.—The object of the experiments was to trace the coagulative process by measuring the concentration of the colloid still in solution after various intervals of time.

Experiments with a similar object have been performed by Miss Chick and C. J. Martin on the "heat-coagulation" of proteins—hæmoglobin and egg-albumen*. This so-called "heat-coagulation" appears to be, first of all, a reaction between protein and water, leading, in the second place, to the precipitation or agglutination of the former. In these earlier experiments the results obtained concerned the first stage only, as the time required for the second was relatively small. More recently, however, by experimenting with denaturated protein, they have been able to study the actual precipitation process—the real coagulation of the substance†. In these later experiments the times which elapsed from the instant of putting the solution to stand, to the first distinct appearing of the precipitate, were noted. The reciprocals of these times give numbers proportional to the rates of coagulation of these substances. It was found that there were temperatures between the limits of which alone coagulation or agglutination was possible. The effect of the addition of electrolytes varied according to the source from which the proteins were obtained. In one case, with the addition of salt, the rate of coagulation increased; in another it decreased. The properties of these solutions seem to be much more complex than those of inorganic colloids.

* *Journ. of Physiol.* July 1910, and Sept. 1911.
† Brit. Assoc. 1911.

In carrying out the experiments with colloidal copper the following method of procedure was adopted. Generally 200 c.cs. of the colloidal solution were introduced into a 500 c.c. Jena glass flask. A known volume of a standard solution of the salt (Na_2SO_4 or NaCl) was then added drop by drop, the contents of the flask being stirred the while to ensure thorough and rapid mixing. When the *hot* method was employed for causing the coagulated particles to settle, the stirring was continued for about two or three minutes, and then the flasks were put aside to stand. From time to time about 35 c.cs. were drawn off into a 100 c.c. Jena flask, heated till close on boiling and placed to stand.

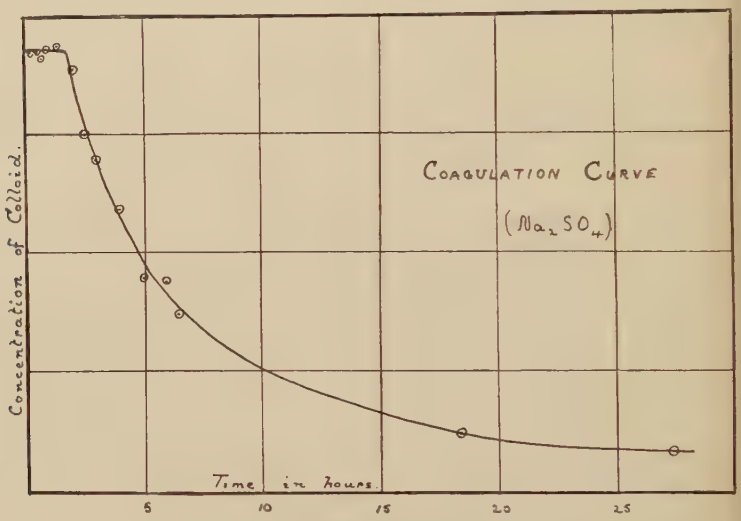


Fig. 1.

When, after a few minutes, the precipitate had settled completely, 25 c.cs. of the clear solution were drawn off and the copper content determined volumetrically. With the *cold* method, gentle stirring was continued throughout the experiment, except that from time to time it was stopped, the precipitate allowed to settle, and 25 c.cs. of the clear liquid drawn off and titrated with the standard nitric acid.

The general results were as follows. For a certain initial period no precipitation occurred. When it set in, it was rapid at first, then becoming slower and slower as shown in the curve (which is one obtained in an experiment with Na_2SO_4).

A certain small amount of coagulated material was always found in the liquid, even during the "initial period." This is due partly, perhaps, to the effect of heating the liquid before the

ortion for titrating was drawn off, but more probably to the fact hat in the addition of the salt solution high concentrations occur n places before the liquids have time to mix thoroughly, with he result that in these localities small portions of the colloid each the condition for coagulation at a high rate. It may be emarked that using the "cold" method such an effect would ot easily be detected. In the early stages of the precipitation he particles are so fine that it is almost impossible to get them o settle in a convenient time.

§ 5. *The Absorption Curve.*

It has been shown* that in the coagulation of colloidal olutions by means of electrolytes the ions which possess charges

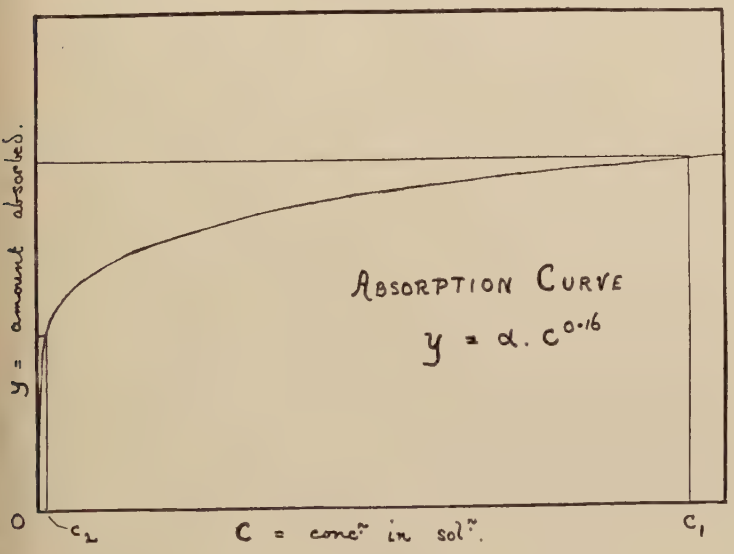


Fig. 2.

pposite in sign to that of the colloid particles are absorbed, and hat for ions of varying valency the absorption takes place in equivalent proportions. Since, for coagulation, very much larger amounts of the salt are required to be added to the solution if the effective ion is monovalent than if it is divalent, and so on, it follows that as we increase the valency of the ions the proportion of them absorbed by the colloid increases also. Thus Freundlich

* Whitney and Ober, *J. Amer. C. S.* 1901, xxiii. p. 842; Freundlich, *Zeit. Phys. Chem.* 1910, lxxiii. 4, p. 385.

found that for a hydrosol of arsenious sulphide containing 1·86 grams of As_2S_3 per litre, 0·093 milligram-molecule of $Al(NO_3)_3$ or $\frac{1}{2}Ce_2(SO_4)_3$ were required per litre for coagulation. The amount of the ions absorbed per gram of As_2S_3 is given as about 0·087 milliequivalent, or 0·162 milliequivalent for 1 litre of the above solution, *i.e.* 0·054 milligram-molecule in the case of a trivalent ion. This would mean that about 50 or 60 °/₀ of the trivalent ions were absorbed by the As_2S_3 in its coagulation, as compared with a small fraction of 1°/₀ in the case of monovalent ions.

The great difference in the percentage absorption and likewise in the "coagulative powers" of ions of different valency has received a satisfactory explanation from Freundlich based on the form of the absorption curve. He found that for the same colloid ions of differing valency were absorbed equally strongly in *equimolecular* concentrations. If then the relative condition for coagulation be that equivalent quantities must be absorbed, it follows from the absorption curve that the concentrations in the solution will differ widely for the ions of different valency.

Thus in the above curve, where the coordinates are expressed in molecular units, if OC_1 represent the solution concentration of monovalent ions required for coagulation, OC_2 will represent the corresponding solution concentration for divalent ions. The equation of the curve is of the form $y = \alpha . c^{\frac{1}{n}}$, and Freundlich found that the value of $\frac{1}{n}$ lay between 0·14 and 0·20 for the different colloids studied.

An example of the working of this hypothesis was found in the coagulation of colloidal copper solutions by means of salts with mono- and di-valent anions (NaCl and Na_2SO_4). The amounts of these salts required to bring about coagulation at the same rate were noted. On Freundlich's hypothesis we have for the monovalent ion

$$y = \alpha . c_1^{\frac{1}{n}} \text{ say.}$$

For the divalent ion (an equivalent absorption) we have

$$\frac{y}{2} = \alpha . c_2^{\frac{1}{n}}.$$

Dividing we get

$$\left(\frac{c_1}{c_2}\right)^{\frac{1}{n}} = 2.$$

Experimentally $1·27 \times 10^{-5}$ gram-molecules of Na_2SO_4 behaved the same as 81×10^{-5} gram-molecules of NaCl in 215 c.c. of th

copper solution. Allowing about one-fifth for the absorption of the sulphate ion (the accuracy of this amount has very little effect on the calculation we are making), the ratio of the two concentrations $\left(=\frac{c_1}{c_2}\right)$ is about 80, whence $\frac{1}{n} = 0{\cdot}16$ approximately. This value is the same as the one, 0·1617, obtained directly by Freundlich for (negative) colloidal gold.

We can extend this result to finding the concentrations *in the solution* of the tri- and tetra-valent ions necessary to bring about coagulation at the same rate. We thus obtain as solutions of the equations

$$(8 \times 10^{-4}/c_3)^{0{\cdot}16} = 3,$$

and

$$(8 \times 10^{-4}/c_4)^{0{\cdot}16} = 4,$$

$c_3 = 8 \times 10^{-7}$, and $c_4 = 1{\cdot}4 \times 10^{-7}$, these being the fractions of a gram-molecule in 215 c.c. of the colloidal solution; for 50 c.c. solution we should obtain

$$c_3 = 1{\cdot}9 \times 10^{-7}, \text{ and } c_4 = 0{\cdot}33 \times 10^{-7} \text{ gm.-mol.}$$

Before the experiments on the rate of coagulation were performed, a number of observations were made on the coagulation of colloidal copper solutions with potassium ferri- and ferro-cyanides, containing tri- and tetra-valent anions. In these latter cases the process seemed to be much more sudden if it took place at all; solutions not quite coagulated at the end of one or two hours, seemed to remain unaltered when left for several days.

Accordingly, experiments with these salts took the form of determinations of the amounts required to produce coagulation when left to stand for an hour or two, the results being apparently the same as those which would have been obtained if the solutions had stood for a much longer time.

The method employed was to titrate the colloidal solution with solutions of the salts. The larger part of the electrolyte was added at the beginning of the experiment and the last few drops much later—the final addition taking place usually two or three hours after the first one. The amount of electrolyte added was deduced from the number of drops from the burette and the average mass of a drop—this method being sufficiently accurate for the purpose, as forty or fifty drops usually were required.

It was found that using colloidal solutions of various concentrations, the dilutions being made by the addition of distilled water, the amounts of ferri- and ferro-cyanide solutions required to produce complete coagulation were nearly proportional to these concentrations. In several series of experiments this proportionality seemed to be exact, though in others it was only approximate, a proportionately larger amount being required for the more dilute solutions.

These results are satisfactorily explained if nearly the whole of the trivalent and tetravalent ions are absorbed by the colloid. The ions are removed from solution; their concentration is suppressed, until, when coagulation has been reached it has only some small value—that required to bring about the actual absorption.

It was found that the amounts required to coagulate 50 c.c. of the colloidal solution varied from 4 to 7×10^{-7} gm.-mols. of $K_3Fe(CN)_6$, and from 3·5 to 6×10^{-7} gm.-mols. of $K_4Fe(CN)_6$.

If we compare these results with those obtained from the absorption curve we notice that the smallness of the concentration of the tetravalent ion in the solution as compared with the total amount added is in agreement with the observation that nearly the whole of the ion is absorbed. This cannot be said, however, for the results of the experiments with the trivalent ferricyanide ion. Moreover, a smaller number of gram-equivalents were required for coagulation with this ion than with the other. It is possible that a chemical change in the $K_3Fe(CN)_6$ would account for the discrepancy. Though these solutions were stored in the dark the experiments were carried out in the light. The sensitiveness of the salt solution to light might have been responsible for a chemical change, or the colloid itself might have had some effect. It was also found that when the coagulated copper was dissolved by the addition of a few drops of sulphuric acid, copper ferrocyanide, $Cu_2Fe(CN)_6$, of characteristic red colour was precipitated, both when the coagulation had been brought about by $K_3Fe(CN)_6$, and also when it had been brought about by $K_4Fe(CN)_6$. No difference could be seen between the two cases. It is as though the trivalent $(Fe(CN)_6)'''$ ion had been converted into the tetravalent $(Fe(CN)_6)''''$. Considering only the results with potassium ferrocyanide ($K_4Fe(CN)_6$), however, we have satisfactory agreement between theory and experiment. These results may then be used as giving some idea of the number of gram-equivalents of *any ion* absorbed by the colloid in coagulation.

§ 6. *The Action of Heat. The "Methods" of Section* 4.

Solutions of colloidal copper may be heated to 100° C. for a short time without any appreciable effect. Prolonged heating (on a water-bath) for about an hour causes coagulation to set in.

A rise in temperature produces a slight increase in the rate of coagulation when sodium sulphate (with a divalent anion) is used as coagulant. The rate of this increase (which was not measured accurately, but which is of the order of a quarter for a change in temperature of 20—30° C.) is very much smaller than that which obtains in chemical action generally. With potassium nitrate

(monovalent anion) there seems to be a retarding effect, but that is due to the fact that warming such solutions causes some of the coagulum to redissolve. In the "hot" method, since the heating of the solution only required about a minute, an increase in the rate of coagulation as just described for sodium sulphate would have but little effect on the result.

That there is no very marked change in the rate of coagulation near 100° C. was found by observing the effect of keeping coagulating solutions on the water-bath for various intervals of time. The longer the heating, the greater the increase in the amount of coagulation; but the effect is not large, so that we may conclude that it could not be of importance in the short time the solutions are heated in the "hot" method. Shaking the solutions at these high temperatures also produces a marked increase in the amount of coagulation.

On comparing the two methods, the "hot" and the "cold," it was found that solutions treated according to the "hot" method showed greater coagulation than those treated according to the "cold." This was partly due to the fact that at ordinary temperatures the flocking together of the coagulated particles did not take place so readily as when the solutions were hot. One had sometimes to wait quite a considerable time for the particles to settle when the solutions were cold. Further, on account of this increased readiness of the particles to flock together at the higher temperature, it is probable that raising the temperature causes particles of a *smaller size* to adhere to one another than would otherwise do so. Then, finally, there is the direct action of heat on the "rate" of coagulation.

In the cold method the continuous stirring increases the rate of coagulation, but the influence of this treatment is not so great as of that we have just been considering.

The advantage of the cold method lies in the fact that heating the solution is avoided. The *clearing* of the liquid when standing to settle is nothing like so effective, however, as when the solution has been heated to boiling. Both methods introduce errors, and hence the interpretation of individual curves is to that extent uncertain. It is important to notice, however, that if the effect of heating the solution differs for solutions coagulating at different rates, it will be more pronounced for the more rapid coagulation—when for example there is a larger concentration of the electrolyte. The stirring effect, on the contrary, will be proportionately larger for the slower coagulations, for here the stirring is more prolonged. The fact that the same results are obtained with both treatments using the method of comparison described in the next section, is powerful evidence that we are able to eliminate the errors of individual curves.

The "hot" method is only trustworthy for coagulation with salts like sodium sulphate containing a divalent anion, since with monovalent anions the coagulation appears to be reversible to some extent, and quite a large amount of precipitate will sometimes go back into solution on heating. Notwithstanding, when the method was actually tried, the comparative results were practically identical with those obtained by the other method, so long as the comparisons made were between solutions of the same colloidal concentration.

§ 7. *Variation of Rate of Coagulation with Concentration of Electrolyte.*

By comparing the coagulation curves obtained with colloidal solutions to which various amounts of salt had been added (so that the rates of coagulation were different), it was found that the abscissae of points with the same ordinate bore a constant ratio to one another for different values of this ordinate; that is, one curve could be made to coincide with another if all the time coordinates were increased (or diminished) in a constant ratio. This ratio, therefore, may be taken as the *rate of coagulation* of the one solution relative to the other. It is the inverse ratio of the times taken by the two solutions to reach the *same stage* in the coagulative process. This is the method of comparison adopted, and is the basis of all the deductions made from the following experiments. The relative times were measured for various parts of a pair of curves, and the mean taken.

The curves of Fig. 3, taken from an experiment with sodium sulphate, show the relation. The results of this series are given in Table I on p. 445. (Expt. I.) The curves show the coagulation with 11·0, 10·0 and 9·0 c.cs., respectively, of the Na_2SO_4 solution.

In this way we avoid to a large extent the errors which the methods (already described) of treating the solutions necessarily entail. So long as the extra coagulation brought about by heating the solutions is the same (or only approximately the same, since we are dealing with very large changes in the rate of coagulation), the results will be unaffected. Corresponding points (referring to the same stage in the coagulation) remain corresponding points if the ordinates are affected equally.

For each series of experiments it is necessary to use from the same *stock* of colloidal solution. Apart from variations in the concentration of copper, the size of the particles, or any other property of them, may vary for solutions prepared on different occasions, and so make it impossible for a fair comparison to be made.

A number of experiments were carried out for the purpose of determining how the rate of coagulation varied with the concentration of the salt. The quantities of colloid used were the same, and the total volumes of the solution were made the same by the addition of the required volumes of distilled water. The amount of salt present was the only variable. It was found that the rate of coagulation increased rapidly with the increase in the concentration of the salt. With each of the two methods of treating the liquid (the hot method and the cold), the relation could be expressed with close approximation by the formula

$$\left(-\frac{dm}{dt}\right) \propto c^p,$$

where m is the concentration of the colloid, c that of the salt, and p is a constant.

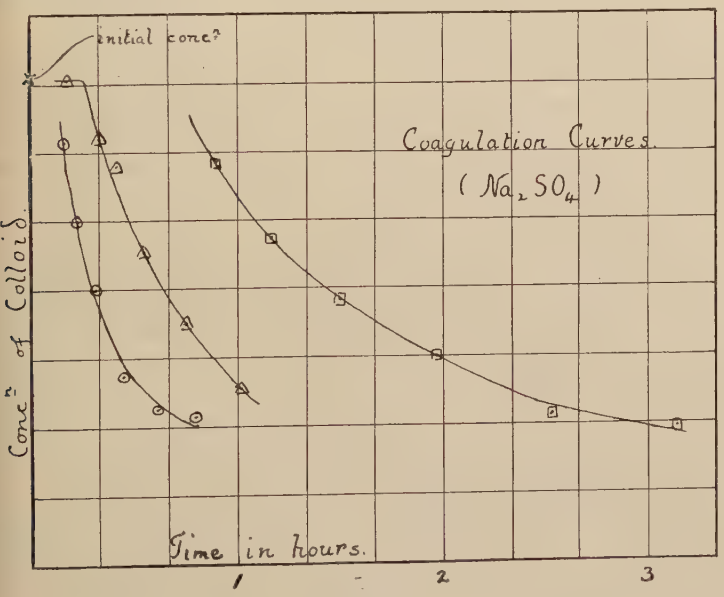


Fig. 3.

Here an important correction must be considered. Some of the anions are absorbed by the positive colloid particles, and are therefore removed from the solution. From Freundlich's results on absorption already cited, we know that for the monovalent ions the relative absorption is small, and need not concern us in the calculation. But for the divalent ions, the fraction absorbed amounts to a quarter or even more of the whole quantity added. For experiments covering but a small range of concentrations of

salt, one obtained a close agreement with the above "power" rule by writing down the total addition of the salt (or anion) for c, only the index p had a higher value; the necessity for making c refer to the concentration *in the solution* was made apparent when experiments over a wide range were carried out. In one series with Na_2SO_4 (using the "hot" method) the solution with greatest concentration of electrolyte coagulated several thousand times as rapidly as the one with least—the one beginning to show a precipitate after about 2 minutes, and the other after about 4 days. In these experiments the results did not follow the "power" rule until the corrections for the absorption were introduced so that c referred to the concentration of the anions *in the solution.*

A further question arises with regard to this absorption. Does the amount of the anion absorbed by the colloidal particles when coagulating vary with the rate at which coagulation takes place, *i.e.* with the concentration of the salt in solution? From the absorption relation $y = \alpha . c^{\frac{1}{n}}$, we should certainly expect that it would. This would mean that the condition for coagulation is *not* that the average absorption should reach some definite minimum value. The accuracy obtained in these experiments was not sufficient to throw any light on this question as the variation to be expected was not large enough.

Unfortunately, the necessity for an absorption correction was not realized until all the experiments had been completed. Consequently it was impossible to obtain an accurate value for this correction, on account of the fact that solutions prepared on different occasions were not comparable for these purposes (owing, for example, to the difference in size and surface of the particles). The method of procedure therefore was as follows. The curve: log (rate of coagulation) : log (concentration of anion) was plotted for the longest series—the one just described. Without the correction for absorption, this is not a straight line. The value of the correction necessary to transform the curve into a straight line was found by trial—both for the case of a constant correction, and for corrections which were related according to the absorption law. This correction was in agreement with the absorption deduced from various experiments with $K_4Fe(CN)_6$ in other solutions.

Table I shows the results for several series of experiments with sodium sulphate and sodium chloride. The 2nd column gives the volumes of the standard salt solution added, and the 3rd the "means" of the curve ratios deduced in the manner already described.

1 c.c. of Na_2SO_4 solution contained $1{\cdot}41 \times 10^{-6}$ gm.-mol. Na_2SO_4.
1 c.c. „ NaCl „ „ $1{\cdot}056 \times 10^{-4}$ „ NaCl.

TABLE I.

Experiment	No. of c.cs of salt solution added	Relative rates of coagulation
I. With Na_2SO_4. 'Hot' method. Total volume = 215 c.c.	5·4	1·00
	5·8	2·30
	6·2	4·91
	6·6	8·15
	7·0	14·7
	7·5	27·9
	8·0	55·4
	9·0	160
	10·0	363
	11·0	755
	12·0	1460
	13·0	2540
II. With Na_2SO_4. 'Hot' method. Total volume = 212 c.c.	7·0	1·00
	7·5	1·73
	8·0	3·23
	8·5	5·75
	9·0	9·5
	9·5	14·2
	10·0	24·5
	10·5	34·7
	11·0	51
III. With Na_2SO_4. 'Cold' method. Total volume = 212 c.c.	8·0	1·00
	8·5	1·36
	9·0	2·24
	9·5	3·27
	10·0	4·56
	10·5	6·2
	11·0	8·3
	11·5	11·1
	12·0	16·3
IV. With NaCl. 'Cold' method. Total volume = 210 c.c.	4·0	1·00
	4·5	2·28
	5·0	3·50
	5·5	6·2
	6·5	11·9
	7·5	26·0
	8·5	41·1
V. With NaCl. 'Cold' method. Total volume = 210 c.c.	4·5	1·00
	5·0	1·76
	6·0	4·78
	7·0	9·0
	8·0	16·6
	9·0	25·6
	10·0	41·2

The following three curves (Fig. 4) were drawn for experiment I. Curve I shows the relation between the logarithm of the rate of coagulation and that of the concentration of the salt uncorrected for absorption. Curves II and III show the same relation after the corrections for absorption had been applied—in the former the correction being a constant quality (= 2·5 c.c.), in the latter the corrections for the various points being related according to the absorption law (varying from 2·65 c.c. for the smallest concentration

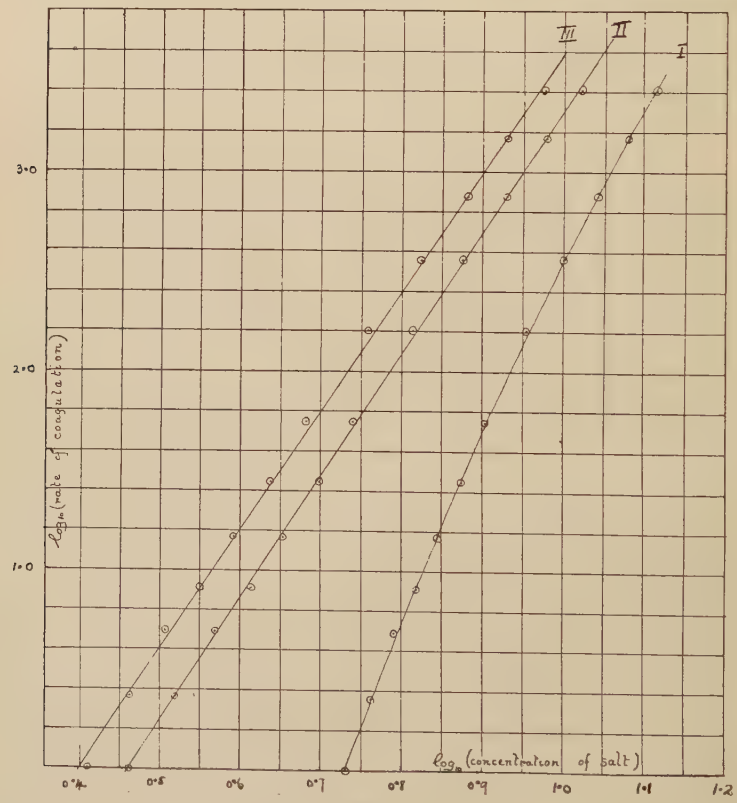


Fig. 4.

to 3·25 c.c. for the largest). It was found that the points lay more nearly in a straight line when the former correction was smaller than the latter. The correction of 2·5 c.c. corresponds to an absorption of $3{\cdot}5 \times 10^{-6}$ gm.-mol. of $(SO_4)''$, *i.e.* about 7×10^{-6} gm.-equivalent. From § 5 we have at once that the absorption of the tetravalent ion in a number of experiments varied from 3·5 to 6×10^{-7} gm.-mol. per 50 c.c. colloidal solution, *i.e.* from 5·6 to $9{\cdot}6 \times 10^{-6}$ gm.-equivalent per 200 c.c.

From the relation $\left(-\frac{dm}{dt}\right) \propto c^p$, we have at once

$$\frac{d \log \left(-\frac{dm}{dt}\right)}{d \log c} = p.$$

Hence, the inclination of the straight lines in Fig. 4 gives us the value of p. We thus have $p = 6{\cdot}0$ for both II and III, these two lines being almost parallel.

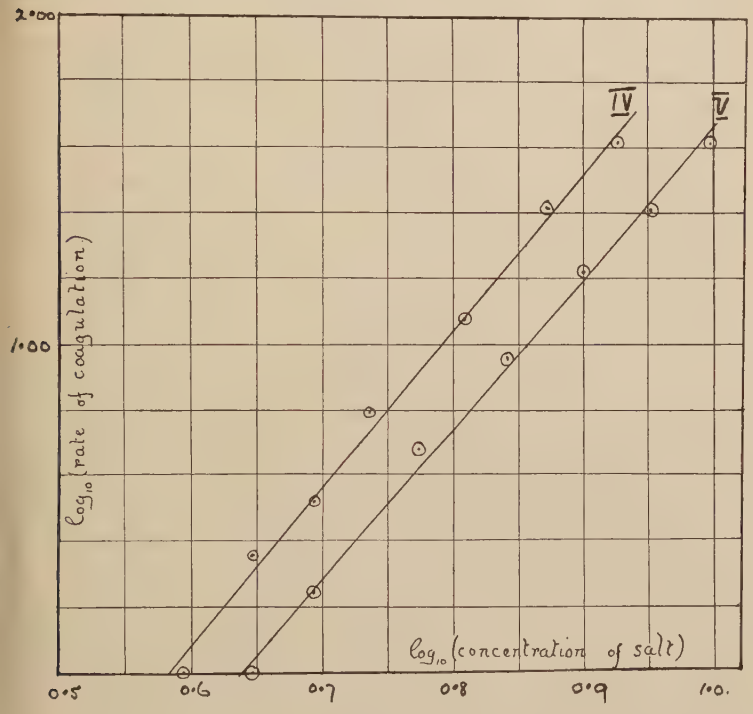


Fig. 5.

For the other two sodium sulphate experiments recorded in Table I, the range of observations was not sufficiently wide to give any definite indication of what the magnitude of the absorption correction should be. Hence the value obtained from the first experiment, viz. 2·5 c.c., was employed. Plotting the logarithms of the rates of coagulation, and of the corrected concentrations, as before, we obtain for the value of p in Expt. II, 6·2, and in Expt. III (where the solutions were treated according to the "cold" method), 5·1.

An absorption of 7×10^{-6} gm.-equivalent (as determined for Expt. I) corresponds to 0·07 c.c. of NaCl solution as used for Expts. IV and V. This small correction (practically negligible) was applied before drawing the corresponding curves for these experiments (Fig. 5). The two values of p given by IV and V are 4·8 and 4·6, respectively.

It will be seen that the index p has about the same value for monovalent and divalent anions. There is a tendency for the results for the "cold" method to show a slightly lower value than those for the "hot." This difference may be due to the fact, that, with the cold method, the particles do not so readily flock together and settle, as with the hot. This apparent lag in the coagulation is more perceptible the more rapid the process—when the periods are short—and consequently the increase in the rate of coagulation with the concentration of the salt appears to be less.

A number of experiments with monovalent anions using the "hot" method gave a value for p close on 6·0, though, as has been already stated, the method would not be trustworthy on its own account.

§ 8. *Variation of Rate of Coagulation with Concentration of Colloid.*

Experiments were carried out with colloidal solutions of various concentrations with a view to determining what influence the concentration of the particles in the liquid had upon the rate of their coagulation. The total volume of the solution was kept constant, and was made up with definite volumes drawn from the stock solution of copper, with the requisite additions of distilled water. The amount of electrolyte added in each case was the same. In this series, comparing solutions of different colloidal concentration, the same *stages* in the process are reached when the same *fractions* of the copper have been precipitated in each case. The rule for the constancy of the time ratio for any pair of curves then holds.

For this series also, a correction for the absorption of the divalent ion had to be applied. Since the concentration of the copper was not the same in all the solutions, the amount of the absorbed part of the salt varied also, and hence the part left in the solution varied in the reverse way. To make the results comparable, the time ratio for each curve was reduced to what it would have been, had the concentration of the anion in the solution itself been the same. This correction was made by means of the results of the previous section.

It was found that for coagulation brought about by the addition of Na_2SO_4 (using the "cold" method) the *times* required for the concentration of the colloidal copper to fall to some particular

fraction of its initial value, were inversely proportional to the initial concentration of the colloid. The actual amount of coagulation taking place in each case is, of course, proportional to the concentration. Hence the rate of coagulation—the rate at which colloidal particles come together—is directly proportional to the square of the initial concentration.

Thus if R represent the mean rate of coagulation over a certain period t, then Rt will be the actual amount of coagulation in this period, and $\frac{1}{m} . Rt$ the fraction of the whole m.

Hence for "corresponding points" we have

$$\frac{1}{m_1} R_1 t_1 = \frac{1}{m_2} R_2 t_2 = \text{etc.}$$

By experiment it was found that

$$t_1 : t_2 : \ldots = \frac{1}{m_1} : \frac{1}{m_2} : \ldots .$$

Therefore

$$\frac{1}{m_1^2} R_1 = \frac{1}{m_2^2} R_2 = \text{etc.},$$

$$\text{or } R \propto m^2.$$

Table II contains the results of several series of experiments which illustrate this. The first column gives the particulars of each series; the second, the amount of original copper solution present in each experiment; the third, the mean "time-ratio" for the coagulation curve (referred to the first one of the series). The fourth column gives these latter values corrected as already described. It was found that the best results, that is, most near to the theoretical ones of the fifth column, were obtained by taking the absorption somewhat less than that obtained in the experiments of the last section, viz. 1·6 c.c. of Na_2SO_4 solution for 200 c.c. of the colloid. This would mean an absorption of the sulphate ion amounting to $4{\cdot}5 \times 10^{-6}$ gm.-equivalent per 200 c.c. of the colloidal solution.

The solutions were treated according to the "cold" method.

1 c.c. Na_2SO_4 solution contained $1{\cdot}41 \times 10^{-6}$ gm.-mol. Na_2SO_4.

With NaCl (using the "cold" method) this relation was departed from. The coagulation with this salt (as also with others containing a monovalent anion) is to a certain extent reversible. If the direct coagulating effect is proportional to the square of the initial concentration, and the reverse effect is simply proportional to the initial concentration, then, since the reverse action does not increase so rapidly with the concentration as the direct one does, the proportionate variation of the resultant coagulation with concentration will be more rapid than is the case with non-reversible coagulation.

TABLE II.

Experiment	Amount of original colloidal solution (c.cs)	Time-ratios		
		Observed	Corrected	Theoretical $\left(t \propto \frac{1}{m}\right)$
I. With 7·0 c.c. of Na_2SO_4 solution. Total volume = 157 c.c.	150	1·00	1·00	1·00
	125	1·02	1·21	1·20
	100	1·12	1·56	1·50
	75	1·15	1·88	2·00
	50	1·78	3·40	3·00
	25	3·25	7·20	6·00
II. With 9·0 c.c. of Na_2SO_4 solution. Total volume = 209 c.c.	200	1·00	1·00	1·00
	150	1·07	1·39	1·33
	100	1·20	2 01	2·00
	75	1·35	2·55	2·67
	50	1·80	3·82	4·00
	25	3·42	8·14	8·00
III. With 6·0 c.c. of Na_2SO_4 solution. Total volume = 156 c.c.	150	1·00	1·00	1·00
	100	·96	1·43	1·50
	50	1·31	3·18	3·00
IV. With 5·0 c.c. of Na_2SO_4 solution. Total volume = 155 c.c.	150	1·00	1·00	1·00
	100	·90	1·48	1·50
	50	1·07	2·78	3·00

[Or thus: If we write R, the rate of coagulation, equal to

$$km^2 - qm,$$

then

$$\frac{dR}{dm} = 2km - q$$

$$= \frac{2km^2}{m} - \frac{2qm}{m} + q$$

$$= \frac{2R}{m} + q,$$

whence

$$\frac{dR}{R} = 2\frac{dm}{m} + q\frac{dm}{R}.$$

For non-reversible action we should have simply,

$$\frac{dR}{R} = 2\frac{dm}{m}.]$$

This is what we actually find in the experiments with NaCl. Thus in one series when the amounts of colloid present in each experiment were 150, 125, 100, 75 and 50 c.cs. of the original solution, the "time-ratios" were 1·00, 1·27, 1·71, 2·32 and 5·6 respectively, instead of the theoretical 1·00, 1·20, 1·50, 2·00 and 3·00. In another series with 150, 100, 75 and 50 c.cs. of the original solution in the several experiments, the "time-ratios" were 1·00, 1·99, 3·09 and 5·9.

Using the hot method with Na_2SO_4, we find that the rate of coagulation varies somewhat more rapidly with the concentration than we should expect from the square law; but this is simply explained if the coagulative effect of the final heating (in this method) be proportional to the square of the concentration, for then it is proportionately greater for the strong than for the weak solution.

In order to complete the study of the rate of coagulation, it was necessary to test whether the presence of coagulated material had any effect. Some of the colloidal copper which had been coagulated with Na_2SO_4 solution, was washed with distilled water in order to free it from excess of electrolyte, and finally shaken with some of the pure colloidal solution. The concentration of this solution was determined before and after. No appreciable effect could be detected. Further, two equal volumes of colloidal solution, to which equal quantities of sodium sulphate solution had been added were studied side by side—being stirred gently all the while. When coagulation set in, 10 c.cs. of the liquid were drawn from each at intervals—in the one case the clear liquid only being removed, and in the other as much of the precipitate

as possible being drawn up into the pipette. In the one case, therefore, the precipitate accumulates rapidly, while in the other it is removed nearly as fast as it is formed. When after some time 25 c.cs. of the clear liquid were drawn off from each and titrated, no difference could be detected as a result of the different treatment. If instead of estimating the solutions by the "cold" method in this way, the liquids were heated at the end according to the "hot" method (the one with a large quantity of precipitate, and the other without), still there was no appreciable difference between the two specimens. The coagulated material is, for all practical purposes therefore, removed from the sphere of action, and takes no appreciable part in the precipitation of the rest of the colloid, in the case when coagulation is brought about by the addition of sodium sulphate (containing a divalent anion).

§ 9. *General Conclusions.*

(i) The "square" law which is found to hold for the coagulative process, as showing the relation between the rate of coagulation and the concentration of the colloid, is in accordance with the principle of *mass action*, and indicates that coagulation is brought about directly by the mutual attraction of the particles. It is inconsistent with any form of condensation of the particles round some other nuclei such as the ions.

The question arises as to what is happening in the solution during the initial stage of the process before precipitation sets in. There are two possibilities: either the time is spent in the absorption of the ions of the electrolyte—coagulation commencing when that absorption has reached some particular value; or else, the absorption taking place more or less rapidly, the particles begin to associate practically at once, but do not attain the size of visible "coagulated" particles till that association has reached some particular stage, after which precipitation sets in.

The evidence is entirely in favour of the second explanation. The comparison of the coagulation curves of § 7 shows that the duration of this initial period is exactly proportional to the duration of any other stage in the coagulation, as though the processes were of the same nature in each. Further, time experiments on absorption, show that this process is completed almost instantaneously*, whereas in the coagulation experiments, the initial quiescent period extended sometimes for several days.

Again, the increase in size of the particles has been found to occur before precipitation sets in. Linder and Picton† observed

* Davis, *J. C. S. Trans.* 1907 (ii.), p. 1666.
† *J. C. S. Trans.* 1895, p. 63.

that the addition of a few drops of very dilute sodium chloride solution to a filterable arsenious sulphide solution rendered it non-filterable, without bringing about coagulation. They also found* that the rate of diffusion of arsenious sulphide solution was sensibly diminished by the addition of an amount of ammonium chloride quite insufficient for coagulation.

They further observed* the process of coagulation under the microscope, a drop of salt solution being brought into contact with the edge of a drop of arsenious sulphide solution under a cover slip. First of all a clear yellow field in the microscope was seen, and then the spreading along of the wave of coagulation. "In the wave front itself the genesis of the hydrogel from the hydrosol was clearly visible; first appeared a dim cloud of vibrating particles too small to be followed with certainty; these rapidly increased in size with proportionately retarded movement, until at a certain critical moment, the granules began to attach themselves to the free surface of the hydrogel and to one another, and all movement ceased."

The actual precipitation, therefore, is associated with the later stages of the agglutination of the particles. But since all the combinations take place at a rate in accordance with the square law, it follows that the rate at which some particular stage in the process, namely precipitation, is reached will also be in accordance with this law—the concentration m in the formula $(-dm/dt) = km^2$ referring to the concentration of the colloid still in solution, for the precipitated portion has been shown experimentally to be inactive (§ 8).

It has already been stated that on account of the treatment of the solutions too much importance could not be attached to the results of individual curves. When, however, the curves were examined, it was found that there was a general tendency on the part of many of them to fit in with the above relation—that is, to satisfy the equation $m(t-\beta) = constant$, deducted therefrom. It seems probable therefore that a more accurate method of experiment would show a closer agreement.

(ii) The explanation of the power rule for the variation of the rate of coagulation with the concentration of the electrolyte does not seem to be at all clear. The expression therefore is for the present merely empirical. It agrees with the experimental results very closely, and for a wide range of velocities of reaction. Viewed at in another way however, the range appears limited. Thus the rate of reaction is proportional to the sixth power of the concentration in the solution, that is, to the thirty-sixth power of the concentration on the colloid particles. In order to increase

* *J. C. S. Trans.* 1905, p. 1906.

the rate of coagulation 3000 times, it is only necessary to increase the amount absorbed by the colloid to $1\frac{1}{4}$ times its previous value.

An interesting coincidence appears in the power rule, for the value of the index p (in $R \propto c^p$) is the same within experimental limits as the index n in the absorption law ($y = \alpha . c^{\frac{1}{n}}$).

The fact that p has the same value for coagulation with ions of different valency (monad and dyad) goes to confirm Freundlich's explanation of the behaviour of the different ions. When equivalent quantities of the ions are absorbed, the particles behave similarly so far as their coming together in coagulation is concerned.

The complex particles so formed, however, have different properties in these various cases, for those coagulated with monovalent ions can be dispersed again, while those coagulated with polyvalent ions show no such tendency. That this difference lies in the nature of these complexes, rather than in the manner in which they were built up, is shown by the following experiment. The precipitate obtained after coagulating a copper solution with sodium sulphate (which shows no tendency to redissolve on washing with water) was digested once or twice with sodium chloride solution (when the absorbed sulphate ions are replaced by the chloride ones). On again washing with distilled water several times, the coagulum is dispersed, exactly as though the precipitation had been brought about directly by sodium chloride. In a similar way the chloride-precipitated coagulum is rendered quite insoluble if first washed with sodium sulphate solution.

The difference in behaviour may, perhaps, be brought about through the possibility of greater concentrations of electric charges in the case of polyvalent ions, whereby the electric forces binding particles together (if indeed such binding forces be electrical) may become more intense than is the case with monovalent ions.

(iii) These experiments with colloidal copper are interesting as demonstrating that coagulation is a definite time-process, which, in some cases, can be traced quantitatively in its various stages. In so far as the properties of inorganic colloids show marked similarities, it is probable that the coagulation of many of them resembles that of colloidal copper, though the appearance of the precipitate may be very different. The method of experiment described in this paper, a method based not so much on the study of individual curves, as on a comparison of these curves over similar stages in the coagulation, would lead one to expect similar results in other cases, especially as these results are fairly simple.

§ 10. *Summary.*

The following is a summary of the most important results obtained in the study of the coagulation of colloidal copper.

1. There is an initial period in which the solution remains clear, and no precipitation takes place.

2. Using colloidal solutions of various concentrations, the rate of coagulation is proportional to the square of the initial concentration ("mass action").

3. For varying amounts of the electrolyte, the rate of coagulation is proportional to some power of the concentration of the anion *in the solution*; *i.e.* a proportionate increase in this concentration results in a proportionate increase in the rate of coagulation.

In conclusion, I desire to thank Prof. Sir J. J. Thomson and Mr W. C. D. Whetham for their kind interest in the above research. The experiments were performed in the Cavendish Laboratory.

Application of positive rays to the study of chemical reactions. By Professor Sir J. J. Thomson.

[*Read* 13 November 1911.]

The author describes the results of the application to chemical reactions of a method which he brought before the notice of the Society at a previous meeting. The production of carbon monosulphide when an electric discharge passes through the vapour of carbon bisulphide was detected by this means. The author gives the results of investigations on the chemical combination between hydrogen and oxygen and hydrogen and nitrogen, and discusses the source of curves corresponding to atomic weights 1—6, 2—5, 20—21, 39, 50—51, which do not fit in with recognised elements or compounds.

Note on the mode of discharge of the Cuverian organs of Holothuria nigra. By G. R. Mines.

[*Read* 30 October 1911.]

The sea-cucumber, *Holothuria nigra*, when irritated emits white conical bodies, the Cuverian organs, which rapidly elongate, shooting through the water while remaining attached at their bases to the animal and forming long, intensely sticky tubes. These are then disconnected from the animal. The elongation of the Cuverian organs has been attributed to internal water pressure by some but by others to an intrinsic activity of the tubes. The former view is strongly supported by the facts presented in this communication. Undischarged Cuverian organs removed from the body cavity of Holothuria can be made to elongate in a manner exactly resembling the normal discharge by injecting them with sea-water or other fluid. The natural discharge of the Cuverian organs is always preceded and accompanied by a rise in the pressure within the body of the animal, and this pressure reaches the value needed to elongate an excised Cuverian organ. The arguments which have been adduced in favour of the intrinsic activity of the Cuverian organs are shown, by further experiments, to lack cogency. An account of this work appears in the *Quarterly Journal of Microscopical Science*, February 1912.

Note.

To the list of Communications made at the meeting of October 31, 1910 (*Proceedings*, vol. xvi. Pt 4, p. 393), the following should be added :

On the Differentiation of Functions defined by Integrals. By W. H. Young, Sc.D.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

The Inheritance of Spirochaetal Infection in Argas persicus. By Edward Hindle, Beit Memorial Research Fellow, Magdalene College, Cambridge.

[*Read* 29 January 1912.]

Whilst working on the morphology of *Spirochaeta gallinarum* at the Institut Pasteur, it was found that the coccoid bodies, which I have described elsewhere (Hindle, 1912), were present in a varying percentage of the eggs laid by infected *Argas persicus*. As these coccoid bodies were found to represent a stage in the life-history of the spirochaete, it became important to determine whether or not the ticks, which hatched out from these presumably infected eggs, produced any infection when they fed on a fowl.

This was all the more necessary as the only observations on this subject, *viz.* those of Brumpt (1909) and Blanc (1911), seemed to show that infection with *S. gallinarum* was not transmitted to the ticks' offspring, and Blanc has used these negative results as an argument against the view that the coccoid bodies (="granules") represent a stage in the life cycle of the parasite.

It was found, however, that if these infected eggs are incubated at 37° C. for about five days, typical spirochaetes may be found in the larvae which hatch out from them. Moreover, all stages may be seen in the elongation of the coccoid bodies up to the ordinary spirochaetal form.

The injection of eggs containing coccoid bodies into fowls and Java sparrows is rarely followed by infection, unless these eggs had been heated to 35° C. for one or two days.

The reason for this is not obvious, but it shows that Blanc is not correct in attaching such weight to his negative results on the infectivity of the coccoid bodies.

Transmission experiments.

The ticks used in the following experiments were part of a consignment kindly sent by Dr A. Foley, from Beni-Ounif- de Figuig, Algeria. They were maintained at a uniform temperature of 28° C. as it has been shown that this temperature is necessary in order for the ticks to produce infection when they bite a fowl. A large number of larvae that had hatched out from the eggs laid by these infected *Argas* were collected and placed on a fowl. After an incubation period of four days the bird became infected and died the next day with its blood swarming with spirochaetes. The fully fed larvae which dropped off this fowl were collected and have been reared to the adult stage. These ticks have been fed only on healthy fowls and yet at each feed they have produced a spirochaetal infection in the bird.

Finally, $4\frac{1}{2}$ months after having been fed as larvae, the ticks have reached maturity and oviposited. Although the eggs have been laid by ticks that have never fed on an infected fowl, yet they contain the characteristic coccoid bodies, showing that the spirochaetal infection in *Argas persicus* may be transmitted to the second generation as well as to the first.

The records of the feeding experiments, given below, seem to show that there is practically no diminution in the severity of the infection the ticks produce at each successive feed.

In all cases the ticks were fed at a temperature of 28° C.

Exp. 1. *Sept. 6th,* 1911.

Several hundred larvae, the offspring of infected parents, were put on to a healthy young fowl. On Sept. 10th the blood of the fowl contained one spirochaete per microscopic field and the following day the bird died, with its blood swarming with parasites.

The fed larvae were collected and kept until ecdysis had taken place, when the first stage nymphs emerged.

Exp. 2. *Oct. 8th,* 1911.

The first stage nymphs from the previous experiment were fed on a healthy young fowl. The result of microscopical examination for parasites was as follows:

Oct. 8th—12th	negative.
„ 13th	1 spirochaete per field.
„ 14th	10 spirochaetes „ „
„ 15th	Died from the disease.

Exp. 3. *Nov.* 13*th*, 1911.

Fed the second stage nymphs from the previous experiment on a healthy young fowl.

Result of microscopical examination:

Nov. 13th—17th	negative.
„ 18th	2 spirochaetes to the film.
„ 19th	numerous „ per field.
„ 20th	„ „ „ „
„ 21st—28th	negative.

The fowl recovered from the infection and did not show any relapse.

Exp. 4. *Jan.* 11*th*, 1912.

Fed the adult ticks from the previous experiment on a normal fowl.

Result of microscopical examination:

Jan. 11th—16th	negative.
„ 17th	10 spirochaetes per field.
„ 18th	numerous „ „ „
„ 19th	20 „ „ „
„ 20th	negative.
„ 21st—26th	„

The fowl recovered and did not show any relapse.

On January 19th, 1912, the first batch of eggs were laid by these ticks and on examination were found to be infected*.

The above described experiments clearly show that once a tick becomes infected with *S. gallinarum* its offspring of the first generation is infective in all its stages, and moreover the infection is transmitted to the second generation. It is evident, therefore, that once the *Argas* of any locality become infected with spirochaetosis it will be very difficult to eradicate the disease.

References.

Blanc, G. R. (1911). "Les Spirochètes." *Thèse de la Faculté de Médecine.* Jouve & Cie, Paris.

Brumpt, E. (1909). "Existence d'une Spirochétose des Poules à *S. gallinarum* dans le pays Somali." *Compt. Rendu Soc. Biol.*, lxvii., pp. 174—176.

Hindle, E. (1912). "On the Life-cycle of *Spirochaeta gallinarum*." Preliminary note. *Parasitology*, iv., pp. 463—477.

* Postscript. The larvae which hatched out from these eggs produced a spirochaetal infection in the fowl on which they were fed. The ticks are being reared in order to see whether the infection is also transmitted to the third generation.

Gregarines in rat-fleas. By C. Strickland, M.A., B.C., Assistant to the Quick Professor of Biology, Cambridge University. (Communicated by Professor Nuttall.)

[*Read* 12 February 1912.]

The gregarine found in the alimentary tract of the larva of *Ceratophyllus fasciatus*, the common rat-flea of this country, leads for part of its life a parasitic existence, and for the other part lives freely in the excrement of this host.

It has all the characters of the group of cephaline eugregarines, and it possesses a symmetrical but complex epimerite, and spores which are regular, oval and unarmed with spines.

The form of its epimerite and spores preclude us from placing it in any of the known families of cephaline eugregarines which have spores unarmed with spines. These families are (1) the *Gregarinidae* with a simple epimerite, (2) the *Dactylophoridae* with complex asymmetrical epimerite and long cylindrical spores, (3) the *Didymophyidae* which inhabit myriapods and form chains of individuals which lose the septum between the proto- and deutomerite, and (4) the *Actinocephalidae*, with cylindro-biconical spores. I therefore propose it be relegated to a new family, the *Agrippindae*, and be named *Agrippina bona*.

The parasite exhibits well-marked nuclear changes.

In the *sporozoite* the nucleus consists of an apparently homogeneous mass of chromatin, but in the earliest *trophozoites* which were found this chromatin appeared surrounded by a clear circular layer of 'karyolymph,' limited by a fine membrane.

Later on the whole nucleus becomes oval, and at one pole appears usually one, sometimes two, small highly refractile spherical bodies, and at the same time the central mass of chromatin becomes less dense in texture and exhibits a skein-like structure. In forms usually a little older than the preceding was sometimes found a refractile body at each pole; but never anywhere but at the poles of the nucleus. In the *sporont* there are similarly one or two of these 'polar' bodies of very variable size, and at the same time the skein of chromatin opens out and forms a single open band which assumes all sorts of fantastic shapes.

When the sporonts have associated to form the cyst the nucleus of each can be seen for only a short time. It is then a very large oval body containing very many of the 'polar bodies' which have multiplied in some unknown way, and the chromatin

band has completely disappeared. As this has gradually been less and less stainable with chromatin dyes, it appears that its ultimate disappearance is due to the absorption of the chromatin.

No further changes can be observed in this nucleus until the *spores* are fully formed, when the eight sporozoites inside the spore can be seen to have each a minute nucleus, consisting of a ring of chromatin. This contrasts with the homogeneous mass of chromatin seen in the free sporozoite.

The above-described nuclear changes are quite different from those described by Wenyon in the relatively closely-allied gregarine, *Lankesteria culicis*.

An experiment to illustrate the mechanical tension on the surface of a charged conductor. By E. F. Burton, B.A. (Cantab.), Associate Professor of Physics, University of Toronto. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 12 February 1912.]

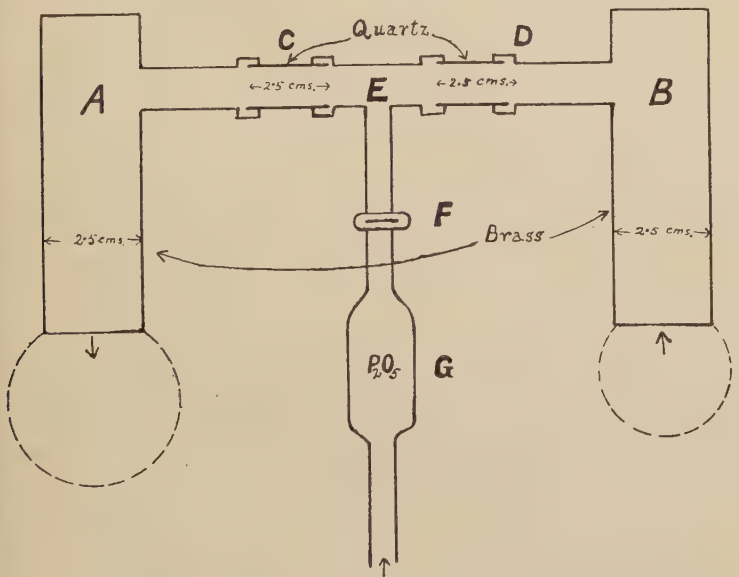
The simple apparatus described below grew out of an attempt to demonstrate experimentally the existence of a real mechanical tension over the surface of a charged conductor. The familiar formula for this tension $\left(\frac{R^2}{8\pi} \text{ dynes per sq. cm.}\right)$ leads to the conclusion that the greatest possible tension on a conductor placed in air at ordinary pressure is about ·3 of a millimetre of mercury*. Such an effect, even on an elastic conductor, would be very difficult to observe directly.

This effect can however be shewn by blowing two soap bubbles, one at each end of a tube, electrifying one of them, and observing the effect of the electrification. The excess of pressure inside a spherical soap bubble over that outside (atmospheric) is equal to $\frac{4T}{r}$. Taking $T = 75$ dynes per cm. (more than for a soap solution), p equals 300 dynes per sq. cm. for a bubble of 1 cm. radius—a pressure of the same order as the maximum electrical tension. One might expect, then, to counterbalance the effects of surface tension in a bubble by putting electrical charges on it. It is well known that if two bubbles are blown on the two ends of a common tube, the smaller bubble gradually blows out the larger one on account of the excess of pressure inside the bubble varying inversely as the radius.

The apparatus designed for the purpose of shewing the effect of electrification is shewn in the figure. Soap bubbles are blown on the tubes A and B which are connected with the central tube EF by means of tubes of fused quartz, C and D. These pieces of quartz serve to insulate electrically the tubes A and B. The air blown into the bubbles passes through a tube G containing phosphorus pentoxide, so that the inside surface of the quartz tubes is kept free from moisture. When the two bubbles are blown simultaneously through the single tube, one of the bubbles will blow slightly larger than the other. If the tube holding the smaller one is electrified by connecting it momentarily to the

* J. J. Thomson, *Math. Th. of El. and Mag.* 2nd ed. 1897, p. 59.

inner coating of a Leyden jar, which is being charged by an electrical machine to some thousands of volts difference of potential between the inner coating and the outer earth-connected coating, it is observed that, under proper circumstances, the smaller electrified bubble is blown out by the larger unelectrified one. The tension due to the electrification tends to neutralise the effect of the surface tension, that is, lessens the effective surface tension, and consequently reduces the value of p inside the electrified (smaller) bubble. Of course, once the larger bubble begins to blow out the smaller the effect is accelerated as time goes on.



There is no virtue in the particular dimensions indicated in the figure. With any particular apparatus, there will be a limit to the size of the bubbles for which the electrical effect (with bubble charged to a given potential) will be large enough to shew the phenomenon indicated above. For a spherical bubble of radius r charged to potential V above the earth the electrical intensity at a point on the surface is given by

$$R = 4\pi\sigma = \frac{4\pi\sigma r}{r} = \frac{V}{r}.$$

Therefore the mechanical tension $\frac{R^2}{8\pi}$ varies as $\frac{V^2}{r^2}$, i.e. inversely as r^2. The mechanical tension on a bubble charged always to a constant potential V decreases rapidly with increase of radius.

If the radii of two uncharged bubbles be r_1 and r_2 respectively, the excess of pressure inside over that outside will be

$$p_1 = \frac{4T}{r_1} \text{ and } p_2 = \frac{4T}{r_2}, \text{ respectively.}$$

$$p_1 - p_2 = \frac{4T(r_2 - r_1)}{r_1 r_2} = \text{approximately } \frac{4T(r_2 - r_1)}{r_1^2} \text{ for large}$$

bubbles.

Therefore, while the electrical effect varies inversely as the square of the radius of the bubble, the excess of pressure in the small bubble over that in the large varies inversely as the square of the radius of either bubble, and, in addition, directly as the absolute difference in the radii. One would expect then that, for a given potential on the electrified bubble, the effect of the electrification shewn by this apparatus would be more apparent with small bubbles than with large. It was found that there was a limiting size for the bubbles (about 3 cms. in diameter) above which the electrification of the smaller bubble due to an electrical machine was not sufficient to reverse the course of procedure observed when neither bubble was charged.

A variation of the above apparatus might be introduced whereby the bubbles on A and B could be blown by separate tubes and only one of the tubes need then be insulated with quartz, because we should be able to blow the smaller bubbles always on either A or B as desired. In any case some experimenting is required to find the most efficient size to which to blow the bubbles. If very small bubbles are used, intense electrification is likely to blow them off the tube A or B.

Radioactivity and Molecular Structures. By W. A. Douglas Rudge, M.A., St John's College.

[*Read* 12 February 1912.]

It is now generally recognised that the radioactivity of Uranium, Radium, etc., is accompanied by some intra-atomic* change, and possibly the radioactivity itself may be due to this change. Many cases are known in which an intramolecular change may be brought about, such as the conversion of oxygen into ozone, ferrous into ferric iron, yellow into red phosphorus, and others too numerous to mention.

In 1907, the writer made some experiments at the Cavendish Laboratory with the object of ascertaining whether these changes were accompanied by a development of radioactivity in bodies usually not radioactive, and as these have not been published, an account of them will be given here. The changes studied were the conversion of magnetic nickel into non-magnetic nickel, and the change from acidic iron into basic iron.

The Nickel Experiments.

These consisted in heating the nickel to a temperature above that at which it remained magnetic, and observing the rate of leak of an electroscope when the current was varied so that the nickel changed from the magnetic to the non-magnetic condition many times per minute. The apparatus used consisted of an electroscope with a plate a few cms. in diameter, and above the plate a close spiral of nickel wire was arranged. The plate and wire were enclosed in a cover of fine copper gauze, and through the gauze a strong magnet passed so as to exert an attraction on the nickel spiral, Fig. 1.

The nickel spiral was heated by the current from a number of storage cells and the strength of the current was adjusted to that value which experiment showed was sufficient to heat the nickel above the critical temperature. This temperature was about 300° C.

The general arrangement is shown in the figure. The outer case was of wood lined with tinfoil and earth connected, apertures being made to enable the gold leaf and nickel wire to be seen. On sending the current through the nickel until the necessary temperature was reached, it was seen that the spiral which curved upwards towards the magnet, when the metal was

* Perhaps intercorpuscular.

in the magnetic condition, fell to a lower position at the moment when the magnetic susceptibility was reduced to zero. By interrupting the current the wire could be kept vibrating as the metal lost or regained its degree of susceptibility. The rate of leak of the electroscope was taken without heating, with heating, and also when it had been heated to a temperature higher than that at which the susceptibility was lost. It could not be heated much higher, as the wire then gave off ions which discharged the electroscope rapidly. The charge given to the electroscope was

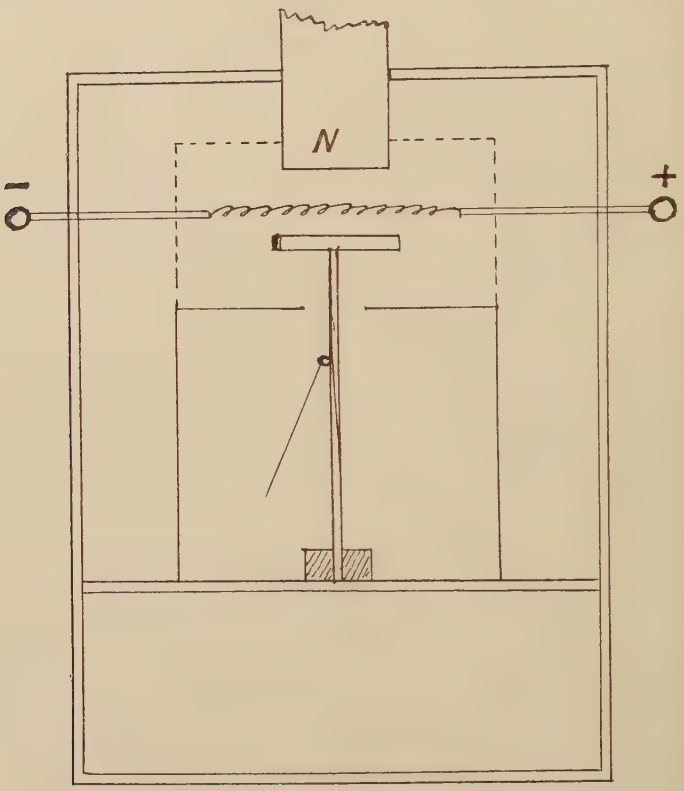


Fig. 1.

sometimes positive and sometimes negative. The rates of leak are shown in Table I.

The rates are practically identical and this result was always obtained, so that it seemed conclusive that during the change from the magnetic to the non-magnetic condition nothing in the nature of a radioactive effect occurred.

Experiments on the corresponding change in iron at about 720° were of course hopeless as at that temperature torrents of ions would be liberated by the heating.

If however anything in the way of an emanation was produced in the process it might be lost by following the method detailed above. The experiment was therefore modified by heating the

TABLE I.

Rate of Leak, without heating.

Time in Mins.	Electroscope Def.
0	50·1
10	49·1
20	48·3
30	47·2
40	46·0

Rate of Leak, wire heated.

Time in Mins.	Electroscope Def.
0	50·0
10	48·3
20	47·8
30	46·8
40	45·9

wire in a closed flask and interrupting the current many times, and then transferring the contents of the flask to the electroscope. The results were negative both with nickel and with iron.

Experiment with Ferrocyanic Acid.

Ferrocyanic acid is one which is very easily decomposed on heating. The iron is present as an acid radicle, but on heating,

hydrocyanic acid is evolved and ferrous ferrocyanide remains; a portion of the iron being changed into the basic form in accordance with the equation

$$3H_4FeCy_6 = 12HCy + Fe_2FeCy_6*.$$

On heating further, a mixture of finely divided iron and carbon remains, which takes fire on coming in contact with the air.

This change occurs to some extent on heating to 100°, but between 100° and 200° the decomposition seemed to be fairly complete when heated in air. At first a small steam heater was arranged in the space at the bottom of the electroscope case, and the acid placed on the top. The rate of leak was

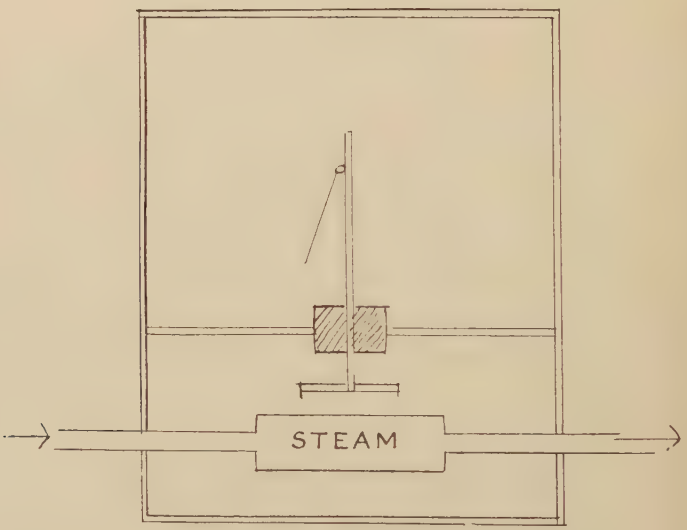


Fig. 2.

determined, before, during, and after heating, but the rate remained the same. The steam chamber was removed and a long spiral of platinoid put in its place and the ferrocyanic acid scattered over it. The spiral was heated by an electric current, which had to be carefully regulated, as if overheated the residue took fire, and then of course the electroscope was at once discharged. It was however easy to adjust the current to prevent this, and at the same time to effect a considerable amount of decomposition. Hydrocyanic acid was freely evolved.

* This equation only represents that portion of the whole change which results in the liberation of HCy.

A number of experiments were made, but with the general result that no change in the rate of leak was observed. The following table is typical.

TABLE II.

Time in Mins.	Reading of Electroscope	
	Without heating	With heating
0	45·5	45·7
10	45·1	45·0
20	44·6	44·5
30	44·0	44·1
40	43·5	43·4
50	43·0	43·0
60	42·4	42·3

These figures show that the rate of leak was not changed during the decomposition of the ferrocyanic acid, but at times some considerable irregularities occurred which could not be traced to any definite cause.

Last year the opportunity presented itself for a repetition of the experiments and in view of further anomalies it was thought advisable to investigate the matter further.

It was observed that the rate of leak was always constant if during the heating a rapid current of air was passed through the apparatus in order to remove the gases evolved during the decomposition, and it appeared that there was a gas present which had the property of discharging the electroscope, that is, the gas was certainly ionised.

A new method of experimenting was devised by which the gas could be introduced into an electroscope and the rate of leak observed when the gas was in the electroscope.

The ferrocyanic acid was prepared from pure potassium ferrocyanide (Kalbaum) by adding pure hydrochloric acid in excess to a saturated solution, filtering through a "Buchner" filter, washing twice with distilled water and drying in a current of warm air. The acid was thus obtained as a nearly white powder, which became slightly blue in the course of a few weeks, and dissolved readily in water.

The arrangement of apparatus is shown in Fig. 3. The electroscope consisted of a 400 c.c. flask silvered on the inside, a portion of the silvering being removed to admit of the gold leaf being observed. The gold leaf system was insulated by quartz and sulphur and could be charged by putting a wire down the quartz tube until it touched the rod to which the gold leaf was attached. The insulation was fairly high. From the electroscope a tube was led to the desiccating arrangement. This consisted of a long U tube filled with phosphorus pentoxide separated into layers by plugs of glass wool. The gauge tube G served to indicate the pressure inside the apparatus. From the drying tube, connection was made with the chamber V_1. This had a capacity of 200 c.c., and was connected to a smaller vessel V_2 in which the acid was heated. The whole could be exhausted by a good mechanical pump down to a millimetre of mercury.

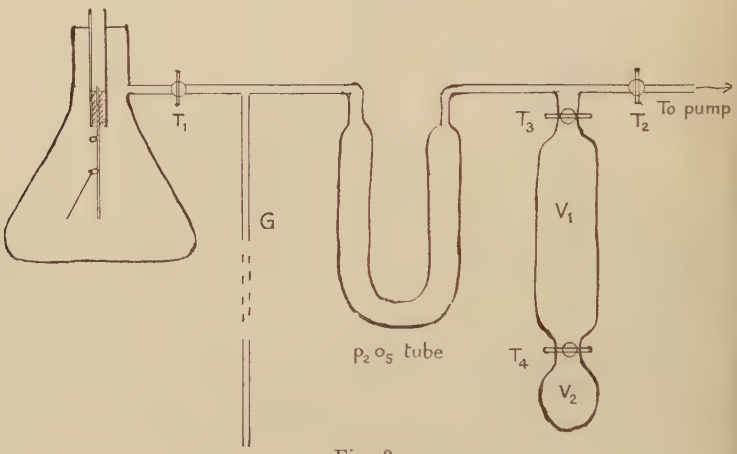


Fig. 3.

The following was the method of conducting an experiment.

The rate of leak of the electroscope was first determined. A gram or so of the acid was introduced into V_2 and the whole apparatus exhausted. T_1 and T_2 were closed, T_3 and T_4 were opened and the acid heated gently until completely decomposed, as was ascertained by the mercury in the gauge becoming stationary. T_1 was now opened and the gas allowed to enter the electroscope. V_2 was removed and by manipulating T_3 and T_4 the gas remaining in V_1 was washed into the other parts of the apparatus, and when the pressure was the same as that of the atmosphere all the taps were closed. Any gas which entered the electroscope was cold and dry; it consisted of a mixture of air and acid.

TABLE III. *Typical case.*

Oct. 5. Natural leak, 22 divisions in 24 hours.
Oct. 6. Gas introduced.

Charge	Time	Deflection	Rate of discharge
	8.15	60	
	8.17	30	15 per minute
New charge	8.17	60	
	8.19	30	15 „ „
New charge	8.20	60	
	8.22	30	15 „ „
New charge	8.23	60	
	8.25	30	15 „ „

The rate of leak of the electroscope was then found; it was enormously increased, i.e. from a rate of *20 divisions a day* to *30 a minute*, and in some cases even more rapid.

Many gases when freshly prepared are certainly in an ionised condition, and therefore are capable of removing a charge, but in the case of the gas, hydrocyanic acid evolved by heating ferrocyanic acid, the ionisation is so strong that it persists for many weeks after preparation and shows at first a fairly uniform rate of decay down to a minimum value.

The increase in the leak was not due to any condensation upon the insulating supports, for if the gas was removed, the rate of leak diminished proportionally to the removal of the gas.

The gas was pumped out, air admitted and the apparatus "washed" out six times by admitting air and re-exhausting.

TABLE IV.

Time	Deflection	Rate of discharge
9.30	60	0·02 per minute
10.30	58·5	
11.30	57·0	
1.0	55·8	

The normal rate of leak is thus nearly the same as on the previous day. Six washings, if the pressure was reduced to 1 mm. each time, were usually sufficient to remove all the activity of the contents of the vessel.

Next day the experiment was repeated under the same conditions, but the gas was not removed and observations were taken over a period of 16 days. The rate of leak became constant in a few days, but was still much higher than if there were no gas present. Table V shows the change in the rate of leak with the time.

TABLE V.

Daily rate for 16 *days.*

During	Average rate in division per minute
1st day	8·1
2nd	0·6
3rd	0·11
4th	0·04
5th	0·03
6th	0·03
7th	0·035
8th	0·0225
9th	0·027
10th	0·03
11th	0·03
12th	0·03
13th	0·03
14th	0 03
15th	0·03
16th	0·03

On the 24th day the electroscope was pumped out and the natural leak was found to be ·0124.

It can be seen that the rate of leak changes very rapidly at first and then reaches practically a steady value.

Fig. 4 gives the average rate of leak during the first twelve hours. A charge was given to the electroscope and the time taken by the leaf to fall through 30 divisions found, and the average value of these rates taken for each hour. The activity thus falls to one-half its value in about two to three hours, but the rate was not always the same in different cases.

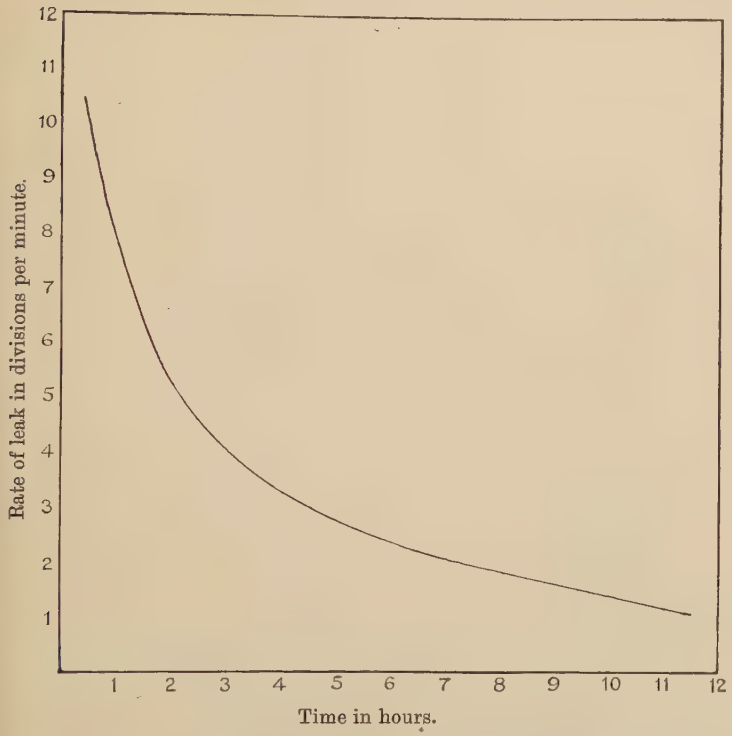


Fig. 4. Curve showing the change in rate of leak during twelve hours.

Fig. 5 shows the change in the rate of leak when the gas was confined in the vessel without any removal for a period of over twenty-six days. It is shortened horizontally, but the rate of leak remained practically constant from the 3rd day until after the 21st.

Fig. 6 shows the manner in which the rate of leak varies with the time. The actual curves showing the rate of leak are a little irregular and therefore it seems best to smooth them out into straight lines, the starting and terminating points being obtained by extrapolation. The figures from which the curves were drawn are given in Table VI.

In the longer periods the leak was allowed to go on through the night. After the first few hours there would not be any great error for comparative purposes, in taking the rate of leak to be a linear function of the time. A fresh charge was given to the electroscope each day, so as to deflect the gold leaf through between 60 and 70 divisions of the eye-piece scale.

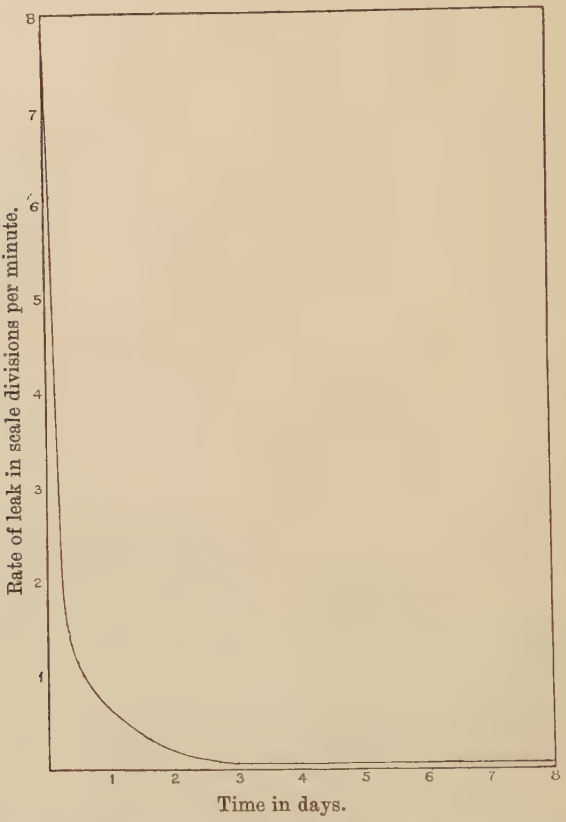


Fig. 5. Change in rate of leak over a period of eight days.

The shape of the decay of activity curve resembles the usual decay curve for a radioactive substance.

These experiments show very clearly that hydrocyanic acid gas evolved by heating ferrocyanic acid is very strongly ionised, and it remains to be shown whether this activity is due to hydrocyanic acid or to the particular mode of preparation. The gas was therefore prepared by the following methods, introduced into the electroscope and tested for its activity:

(1) By heating a cyanide with sulphuric acid.
(2) „ „ a ferrocyanide with dilute sulphuric acid.
(3) By heating mercuric or silver cyanide with sulphuric acid.
(4) By passing sulphuretted hydrogen over mercuric cyanide.
(5) By heating ferrocyanic acid with sulphuric acid.

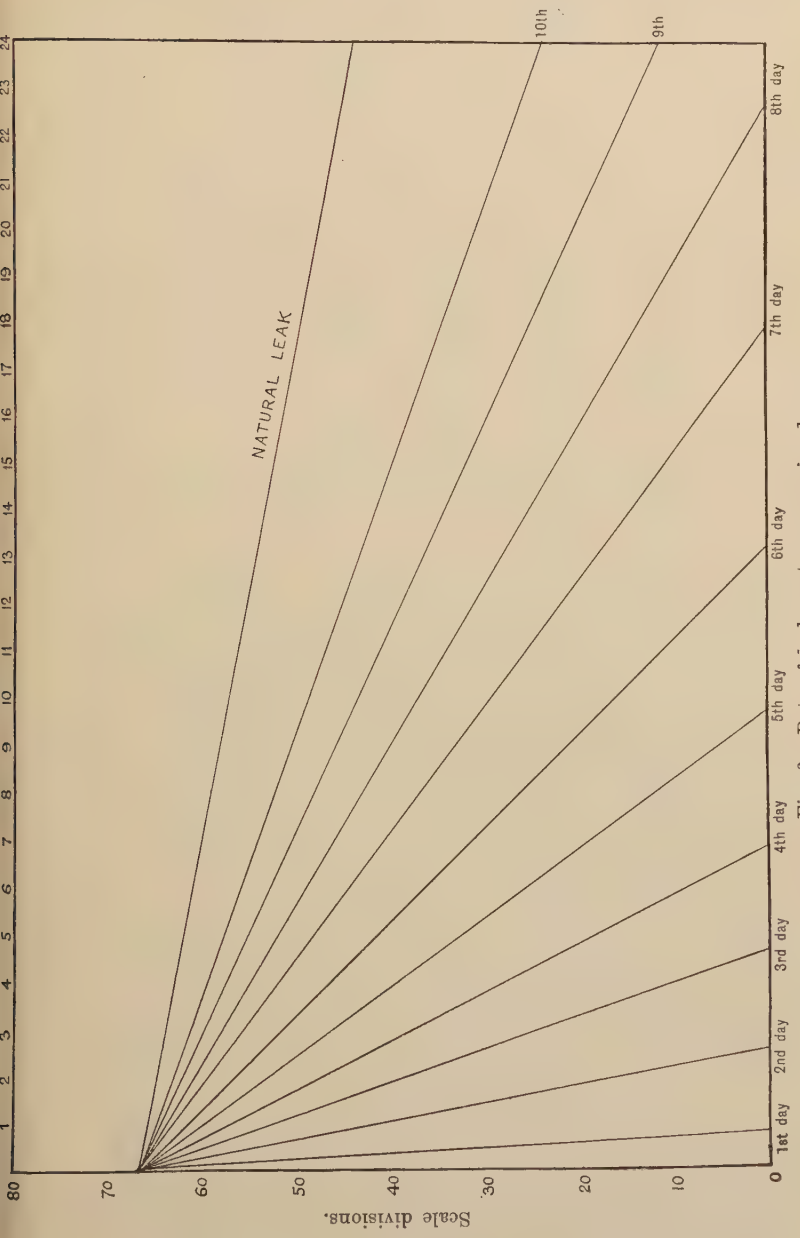


Fig. 6. Rate of leak on ten successive days.

(6) By heating potassium ferrocyanide with strong sulphuric acid. This gives a mixture of carbonic oxide and hydrocyanic acid.

(7) Cyanogen obtained by heating mercuric cyanide was also used.

TABLE VI.

1st day		5th day		9th day	
Def.	*Time*	*Def.*	*Time*	*Def.*	*Time*
67	12.0	67	10.0	68	6.40
60	12.5	60	11.5	45	20.0
55	12.8	52	12.15	39	23.30
50	12.11	47	13.0	28	30.30
45	12.14	44	13.30		
40	12.20	40	14.0		
35	12.27	33	15.5		
30	12.35	30	17.30		
23	12.50				
2nd day		6th day		10th day	
67	6.32	62	4.0	63	6.30
41	7.28	58	5.20	41	20.0
36	7.54	33	79.0	38	22.20
26	9.7			34	44.45
3rd day		7th day		Pumped out 6 times	
66	6·37	66	4.10	64	5.25
63	6·47	38	18.50	50	19.0
56	7.50	36	20.30	40	30.0
52	8.10	32	24.40		
41	10.30				
36	11.55				
20	17.20				
4th day		8th day			
63	7.40	62	6.40		
55	9.11	41	19.0		
47	11.25	38	20.30		
42	12.45	32	24.40		
31	17.45				

In none of these cases was there any unusual activity shown by the gas and therefore it must be concluded that the activity developed was due to the particular method of preparation.

When the gas was generated by the action of sulphuric acid on potassium cyanide the following results were obtained:

Deflection	Time	Rate of discharge
60	0 hour	
58	2 „	
40	14 „	
37	15 „	1·4 division per hour
32	20 „	

The gas was pumped out and the electroscope washed out six times with air and the new rate observed:

Deflection	Time	Rate of discharge
63	0 hour	
60	2.5 „	
54	7.5 „	1·44 division per hour
50	9 „	

The gases evolved by heating strong sulphuric acid with potassium ferrocyanide:

Deflection	Time	Rate of discharge
65	0 hour	
63·5	1.40 „	
61·5	3.80 „	1·36 division per hour
50	11 „	

Gas evolved by heating mercuric cyanide:

Deflection	Time	Rate of discharge
61	11.20 hours	
60·5	11.40 „	
60	12.10 „	
59·5	12.40 „	1·44 division per hour
58	1.30 „	
55·5	3.20 „	

The hydrocyanic acid from the other sources gave similar results, and the activity found for the gas evolved by heating ferrocyanic acid is peculiar to that method.

The electroscope was usually charged with negative electricity, but it was observed that the rate of leak was greater with a positive charge, as the following shows when a small amount of gas was present:

Natural leak	Charge +	Charge −
0·0166 per min.	0·0345 per min.	0·031 per min.

and repeated observation confirmed this, so that the gas seemed to have an excess of negative ions.

The residue left after the expulsion of the gas was next tested to see whether it had retained any charge, and this was found to be the case. An electroscope with a chamber in the bottom in which the material could be placed was used The natural rate of leak was determined for positive and negative charges.

A gram of the ferrocyanic acid was heated in an exhausted hard glass tube until it was judged that the decomposition was complete, and after cooling down to the air temperature the residue was placed on a watch glass and then introduced into the electroscope.

The rate of leak of the electroscope before introduction of the residue and afterwards with the charges was as follows:

Natural	Charge +	Charge −
0·021	0·14	0·20
	0·0415	0·057

The rate of leak is not very much changed but the effect persisted for some time afterwards, and in some instances a measureable amount of activity remained after several days, that is the residue must be giving off positive ions.

This statement is however made with reserve, as the experiments were rather capricious, and requires further investigation.

The excess of positive ions obtained from the residue was far less than the excess of negative in the gas.

That there was an excess of negative ions in the gas was shown by the very different rate of leak of the gold leaf according as the charge was positive or negative.

Some of the acid was heated in a glass flask in which the rate of leak of the gold leaf system had previously been determined. On cooling the gas and introducing the gold leaf system the rate of leak was found to be

	Positive charge	Negative charge
(1)	10 divisions per min.	2·4 divisions per min.
(2)	1·5 „ „	0·75 „ „

Natural leak 0·021 divisions per min.

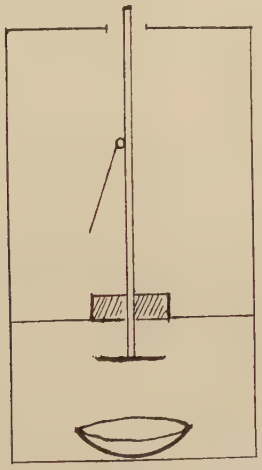


Fig. 7.

The residue was removed by shaking in such a manner as to prevent the escape of the gas, but the rate of leak was not sensibly changed.

Experiments were made in order to determine whether the activity could be removed in the usual way from the gas and whether the activity was due to any kind of emanation.

The gas before entering the electroscope was passed through a U tube 40 cm. in length, plugged with dry cotton wool.

The gas however retained its activity, but if the cotton wool was damp then the whole of the activity was destroyed. This is no doubt due to the solubility of the gas in water.

The wet cotton was quickly transferred to the interior of another electroscope when it was found that some of the activity was retained by the wool, not much however.

Passing the gas into water, it was completely absorbed and the solution showed no trace of activity. Similarly if the gas was submitted to an electrostatic field, the whole of the activity was quickly removed.

Observations were taken with other compounds in which a change from acidic to basic form occurs. For example, potassium bichromate contains the chromium in the acidic form, but by heating with reducing agents, such as oxalic acid, it may be reduced to the basic form with evolution of carbonic acid. A quantity of dried bichromate and oxalic acid were heated in a tube and the fumes evolved passed into the electroscope. No change in the rate of leak was observed. The action in this case is not so simple as in that of the ferrocyanic acid. Potassium bichromate does not decompose on heating alone, and the carbonic acid comes from the oxalic acid, but at the same time the acid oxide of chromium is reduced to a basic one. Potassium permanganate, heated alone or with reducing agents, failed to give any active gas.

Summary.

A number of physical and chemical changes have been studied in which we may reasonably assume that some intramolecular changes occur, and these changes are not accompanied by any effect of a radioactive character.

Hydrocyanic acid gas when prepared by heating ferrocyanic acid is very strongly ionised and the ionisation shows a rate of decay which is similar to that observed in a radioactive deposit, but save in the respect of being highly conducting it does not resemble a radioactive emanation. The residue left after heating ferrocyanic acid has the power of ionising air and retains this for quite a long period.

Some Observations with Dark-Ground Illumination on Plant Cells. By S. Reginald Price, B.A., Clare College, University Frank Smart Student in Botany. (Communicated by Professor Seward.)

[*Read* 26 February 1912.]

The use of methods of Dark-Ground Illumination for high power work in Biology is a fairly recent development. As is well known the method serves to demonstrate the presence of particles and structures which are ultramicroscopic, that is to say below the limits of vision in the microscope with direct illumination. Little has been recorded concerning the structure of the plant cell observed by this method, besides the observations of Gaidukov*.

The principle of the method is now becoming fairly widely known and will not be described here in detail†. The chief points to bear in mind are that the direct illuminating beam does not enter the objective system, but that the structures in the microscopic field become visible by the light which they scatter, portions of the field which are without objects or particles appearing black. Particles which are of ultramicroscopic size may thus indicate their presence by diffraction images.

Structures which on account of their transparency and small size are difficult to observe in direct illumination, especially in living material, are often more easily studied by this method. A good example of this is furnished by the "sap particles" described below, which although of microscopic dimensions, are very difficult to observe in direct illumination.

In the observations recorded below, the Dark-Ground Illuminator has taken the form of a Paraboloid Condenser, designed by Siedentopf‡ and supplied by Zeiss. This is used as an immersion system, water being found the most satisfactory fluid for this purpose, as recommended in the Zeiss prospectus§. The glass object slides must be of good quality and must be specially cleaned, and the absolute cleanness of the cover glass is most important for the best results. Both dry and immersion objectives have been employed. In conjunction with the latter special stops, which drop into the objective above the lens system, have

* Gaidukov, N., *Ber. d. d. Bot. Ges.* 1906, several papers; *Dunkelfeldbeleuchtung und Ultramikroskopie in der Biologie und in der Medizin*, Jena, 1910.

† See Thirkill, H., *Sci. Prog.* 1909–10, iv. pp. 55 sqq.; Siedentopf, *Zeit. f. wiss. Mikros.* xxiv. 1907, pp. 13—20, etc.

‡ Siedentopf, *Zeit. f. wiss. Mikros.* xxiv. 1907, pp. 104—108.

§ Zeiss, *Pamphlets*, 'Mikro. 230,' 3rd Ed. 1910.

to be used, to cut out the peripheral rays which enter the objective when the immersion fluid is present.

The 3 mm. and 2 mm. Apochromats of Zeiss with oculars 4, 6, 12 and sometimes 18 have been employed, as well as a $\frac{1}{4}''$ Parachromatic of Watson. A Nernst lamp is a fairly efficient source of illumination for many cases, but only permits of the lower powers being used. Sunlight is by far the most efficient, and at the same time the most fickle illuminator. It reveals structures and particles which are quite invisible with weaker sources of light. As the following observations are rather of a preliminary nature, no summary of Gaidukov's work will be attempted here.

Elodea canadensis. I have found the cells which occur at the leaf edge of this common water plant, very favourable for observation. At the edge the leaf is one cell thick only, and moreover the cells contain relatively few chloroplasts. The cell wall also is clear and optically homogeneous. A low power examination reveals the presence of numerous particles or rather bodies in the cell vacuoles, briefly referred to hereafter as "sap particles*." They can be seen in nearly all the cells of the leaf, and in most cases are quite within the limits of observation with direct illumination. They are however much more obvious when observed by the Dark-Ground method. They vary greatly in abundance in different leaves, probably according to conditions, maturity and so on. They exhibit an oscillatory or dancing motion almost certainly of the nature of a Brownian Movement.

Higher power examination shows these particles to be usually rod or disc shaped, while there also appear to be forms of a different nature with the appearance of spherical vesicles or bubbles.

The protoplasm itself also exhibits numerous, very minute particles, almost certainly of ultramicroscopic size which appear as bright points of light, quite similar to the particles observed by Gaidukov and others. They show a rapid oscillating motion at first. As the leaf becomes warmed on the stage of the microscope, gradually the streaming and rotation of the whole protoplasm sets in. The rotation and streaming become very obvious quite apart from the motion of the chloroplasts, which remain motionless for some time. The particles pass along with what appears to be a comparatively considerable velocity. At the same time they probably perform their oscillating or Brownian Movements, the protoplasmic layer being filled with these twinkling points of light.

After a time the protoplasm seems to acquire sufficient energy to move the chloroplasts, although in some cases this stage does

* Cf. Gaidukov, *loc. cit.* p. 50, etc.

not seem to be reached. The chloroplasts apparently do not move as rapidly as the protoplasmic stream itself.

The nucleus can often be seen but rather indistinctly as a lenticular mass usually close against one side of the cell. It appears to be optically homogeneous or nearly so, and clear, but on account of the protoplasmic stream which continually passes around it, good observation is difficult. More favourable opportunities may therefore reveal some structure in this nucleus.

In most cases so far observed, the cell also contains a roughly spherical body or aggregation, which appears very bright against the dark ground, being hence of a highly refractive or solid nature. It appears to be composed of motionless particles. In the first place it was mistaken for the nucleus. It can of course be observed in direct illumination, but as yet nothing can be said as to its nature. As the protoplasm begins its rotation, this body also acquires a slow rolling motion and slowly travels up and down the vacuole of the cell, apparently dragged by the protoplasmic stream.

The sap particles continue their Brownian Movement, independently of the rotation of the protoplasm, thus confirming the surmise that they are present in the vacuole and not in the protoplasm itself.

Spirogyra. Spirogyra is also quite suitable for investigation by this method, and the structure presented has been described by Gaidukov*. Sap particles and the small protoplasmic particles are mentioned, the former sometimes visible in direct illumination.

There appear to be two kinds of protoplasmic particles however, differing chiefly in size and forming definite layers of the parietal protoplast of the cell. The relative position of the various particles is determined by taking observations in different planes of focus. The most obvious and at the same time the larger protoplasmic particles come into focus above the chloroplast, that is to say they occur in the protoplasm outside the chloroplast. In a lower focus, more numerous and much smaller particles are seen, forming probably an inner layer to the protoplast. Plasmolysis experiments (which will not be discussed in detail in this short account), seem to reveal moreover, a similar layer containing small particles on the outside, that is to say in contact with the cell wall. This outer layer can usually be demonstrated by subjecting a filament to rapid plasmolysis with dilute glycerine. If the right concentration is chosen the protoplasm is not killed for some time at any rate and movement of particles continues. The chloroplast and the larger mass of protoplasm aggregate towards the centre, where the larger particles can be seen on the outside. In contact with the wall, and sometimes connected by fine protoplasmic

* Gaidukov, *loc. cit.* p. 52.

filaments with the main mass, a layer containing very fine particles in rapid movement can usually be recognised.

The sap particles come into focus in a lower plane than any of these protoplasmic particles, and lie within the vacuoles in plasmolysed cells.

In some cases the nucleus has been observed, though as a rule it is not possible to determine its structure at all accurately. It appears to be fairly transparent though Gaidukov states that it contains numerous small particles*. The suspending threads of protoplasm are clearly seen merging into the layer of cytoplasm which surrounds the nucleus. The threads and this layer outside the nucleus contain the larger protoplasmic particles. They show the usual oscillatory movement, and also move to a certain extent along the threads away from or towards the nucleus.

Most of the foregoing observations have been made on a species of Spirogyra with wide cells and a fairly close spiral chloroplast, so that the motion of the sap particles does not interfere to a great extent with the observation of the peripheral regions of the cell.

Hairs of Tomato. The multicellular hairs which occur on the leaves and stems of the Tomato (Solanum Lycopersicum L.) show the movements very well. They are removed with a piece of the epidermis and mounted in water.

A low power reveals the presence of numerous sap particles, as usual in rapid motion, and these also occur in the epidermal cells of the leaf and stem. With the Nernst lamp as illuminator little is seen but the sap particles and an indication of some protoplasmic movement. In sunlight with the 3 mm. Apochromat and oculars 6, 12 and 18 the following structure is revealed.

The wall is not homogeneous, but shows scattered bright spots of light, with however considerable dark spaces. On focussing down, just within the wall, there occur very minute particles with a rapid Brownian Movement. Lower still, but certainly still in the protoplasm, and forming a second protoplasmic layer, larger particles come into the field. Finally in the vacuole the much larger sap particles occur. They are elliptical or rod-shaped, much as in Elodea, so that they are probably of the same general nature. It seems possible that these sap particles increase in number, with lowering of vitality of the cell in most cases.

Hairs taken from a dead plant show no movement, and the protoplasm seems to have coagulated into a mass full of bright, relatively large particles.

It may be said generally that death of the cell results in cessation of protoplasmic movement.

Mustard Root-hairs. Root-hairs seemed likely to be useful

* Gaidukov, *loc. cit.* p. 52.

objects, and to ascertain their structure, Mustard seeds were germinated on damp blotting paper, so that the hairs were quite clean. Sunlight was used as illuminant.

The wall of the hair is quite transparent. The protoplasm is irregularly distributed within the hair, occurring as "plugs" of various sizes along the long root hairs. Towards the tip the protoplasm is rather more abundant. The protoplasmic plugs show some motionless and some rapidly oscillating particles, the latter appearing the larger. In each plug the motionless particles seem to predominate in that part towards the basal end of the hair, while the distal end of each seems to be almost entirely composed of particles in rapid motion. This was so obvious that it was possible to determine in which direction the apex of a long hair lay, although neither extremity was in the field, and there was practically no variation in diameter. No good indication was obtained of any protoplasm being present in the spaces between the plugs, even lining the cell wall.

There were few particles which appeared to be comparable with the sap particles already described. Scattered particles do occur, especially in the dark spaces, and exhibit a slight wandering motion. They are quite minute, probably below the limits of resolution with direct illumination. In Dark-Ground illumination they appear to have the nature of vesicles or bubbles of some nature.

The above examples of plant cells have been briefly described as having been found to be favourable objects for examination by this method. Others have been described by workers already mentioned. It is not to be assumed that the facts of structure presented are the same for all plant cells, as this is almost certainly not the case. Although theories of protoplasmic structure based on observations made by this method have been advanced, they will not be discussed here, in fact it would seem that more extended observations as well as further experiments on the reactions of protoplasm in different cases are required, before any general theories can be advanced. It has however been fairly well indicated that protoplasm partakes of the nature of a colloidal solution*.

Nearly all the work above described has been done in the Cambridge Botany School. It is my pleasure to thank Prof Seward as well as many others for the kindly interest taken in the work.

* See Gaidukov, *loc. cit.* pp. 60 sqq.

The Variation of Magnetic Susceptibility with Temperature. By A. E. Oxley, B.Sc. (Lond.), B.A., Trinity College.

[*Received* 2 March 1912—*Read* 11 March 1912.]

In 1895 Prof. Curie* experimented on the influence of temperature on the magnetic properties of a number of substances. He found in general that as the temperature was varied diamagnetic substances behaved differently from para-magnetic substances, and this led to the conclusion that the origin of diamagnetism is different from that of para-magnetism.

A few years later, Langevin† developed a theory of magnetism and he showed that so long as we confine ourselves to gases, the experimental laws of Curie can be established on theoretical grounds. A theoretical deduction of Curie's law for para-magnetism had previously been given by Prof. du Bois‡.

An extension of Langevin's theory to include para-magnetic solids has been given by Weiss§.

Still more recently an investigation to examine whether Curie's laws admit of the wide generalisation assigned to them has been carried out by Profs. du Bois‖ and Honda¶.

These physicists experimented at room temperature and found the variation of susceptibility with atomic weight for about fifty elements. Then each element was investigated separately and a temperature-susceptibility curve obtained. From an examination of these curves Honda finds that the effect of a slight increase in temperature on the magnetic susceptibility of an element is the same as that which would be produced by a slight increase in the atomic weight of that element**. According to Honda there is no distinction, apart from sign, between para-magnetism and dia-magnetism, and both he and du Bois consider the basis of Langevin's theory to be unsound.

* *Ann. de Chim. et de Phys.* (VII.) v. 1895, p. 289.
† *J. de Phys.* IV. 1905, p. 678; *Ann. de Chim. et de Phys.* (VIII.) v. 1905, p. 70.
‡ *Arch. Néerl.* (II.) v. 1900, p. 246; VI. 1901, p. 581.
§ *C. R.*, t. 144, 1907, p. 26.
‖ H. du Bois and K. Honda, *Versl. Kon. Ak. v. Wetensch.*, Amsterdam, XII. 1910, p. 596.
¶ K. Honda, *Ann. der Phys.* IV. 32, 1910, p. 1027.
** *C. R.*, t. 151, 1910, p. 511.

The object of the present paper is to make an attempt to reconcile the results obtained by du Bois and Honda with Curie's laws on the assumption that the latter are true for substances composed of simple molecules.

The variation of para-magnetic susceptibility with temperature.

If we take the simple Curie formula:

$$\chi = \frac{C}{\vartheta}$$

where χ is the susceptibility, ϑ the absolute temperature and C Curie's constant, then since C is essentially positive $\frac{\partial \chi}{\partial \vartheta}$ must be negative, and the para-magnetic susceptibility of an element must fall as the temperature rises. This is not in accordance with observations on many elements.

An examination of the structure of pure elements in the solid state, *e.g.* the metals, shows that they are built up of crystalline aggregates each of which is formed by groups of molecules. The axes of the crystals are distributed at random, because on the application of strain the slip bands which are very nearly parallel for one crystal vary from crystal to crystal in an arbitrary manner. Such complex molecular groupings have been shown to exist in zinc, bismuth, iron, cadmium, tin, lead, silver, copper, gold and nickel. In a later research Ewing and Rosenhain* investigated the effect of heat on the crystalline structure. No arrest-points were found for lead similar to those which exist in the case of iron, although a careful search was made for them. Since the slip bands for any one crystal are parallel it follows that each crystal is built up of a system of molecular groups which are similar and similarly orientated. Moreover these systems of molecular groups break up and redistribute their axes as the temperature varies.

The existence of complex aggregates in general in the solid state is considered by J. J. van Laar† in a recent research.

In the following we are concerned with small susceptibilities only, *i.e.* the ferromagnetic elements are excluded.

Let there be N types of molecular groups and denote a particular type by p. If C_p is the corresponding Curie constant, per particle, then the specific para-magnetic susceptibility of the substance may be written:

$$\chi_P = \sum_{p=1}^{N} \frac{n_p \cdot C_p}{\vartheta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

at any temperature ϑ, where N_p is the number of particles of type p which are found in unit mass. The association of the

* *Phil. Trans.* A, CXCIII. 1900, p. 353.

† *Versl. Kon. Ak. v. Wetensch.*, Amsterdam, XII. 1910, p. 26.

molecules to form complex groups is supposed to be a chemical effect and the molecular field is assumed to be negligibly small everywhere. Under these conditions the summation on the R.H.S. of (1) is valid.

Since n_p depends upon ϑ, we may write

$$n_p = n_{0p} \cdot F_p(\vartheta)$$

where $F_p(\vartheta)$ is the function of the temperature according to which a group breaks up as the temperature ϑ varies, and N_{0p} is the number of particles of type p at the temperature ϑ_0 given by:

$$F_p(\vartheta_0) = 1.$$

Equation (1) may now be written

$$\chi_P = \sum_{p=1}^{N} n_{0p} \cdot C_p \cdot \frac{F_p(\vartheta)}{\vartheta}.$$

and so

$$\frac{\partial \chi_P}{\partial \vartheta} = \sum_{p=1}^{N} n_{0p} \cdot C_p \cdot \frac{\partial}{\partial \vartheta}\left(\frac{F_p(\vartheta)}{\vartheta}\right) \quad \ldots\ldots\ldots\ldots\ldots(2).$$

Now any factor of the type $n_{0p} C_p$ is positive while the last factor $\frac{\partial}{\partial \vartheta}\left(\frac{F_p(\vartheta)}{\vartheta}\right)$ may be positive or negative according to the nature of the function $F_p(\vartheta)$.

In the case of the change from para-magnetic "γ" iron to "δ" iron an increase of temperature produces a more complex type of particle. The general effect of an increase of temperature will be to produce simpler particles.

The aggregation probably alters the nature of the internal motions in the atom but this is not essential for the present. It does affect the number of molecular collisions and thereby indirectly affects the para-magnetism of the element.

Hence, according to the manner in which the individual aggregates of the molecules break up, $\frac{\partial \chi_P}{\partial \vartheta}$ may be positive, zero or negative.

The most remarkable variations in the value of $\frac{\partial \chi}{\partial \vartheta}$ are shown by tin*. If the dia-magnetic grey tin is gently heated the specific susceptibility changes almost suddenly with the density and at 35° passes through the value zero. Further heating continually increases χ, and the value $+0{\cdot}03 \cdot 10^{-6}$. for para-magnetic tin is attained at 50°. The value at χ now remains constant until the melting point at 232° is reached where there is a discontinuity

* H. du Bois and K. Honda, *loc. cit.* p. 602.

and it falls to $-0{\cdot}04 \,.\, 10^{-6}$, the dia-magnetic liquid retaining this value unchanged on further heating. Du Bois and Honda consider these irregularities to undermine the assumptions made in Langevin's theory. Nevertheless Honda's rule will not account for them, while there is every possibility that they are fully accounted for if we consider the change in the constitution of the molecular groups owing to changes in density and alteration in crystalline form.

The variation of dia-magnetic susceptibility with temperature.

That the dia-magnetic susceptibility of many substances varies with the physical state is clearly shown by du Bois and Honda*. For instance they find a difference in allotropic form is accompanied by a change in susceptibility in phosphorus, antimony, carbon, and tin. Also there is a discontinuity at the melting point in the case of P (44°), Ag (961°), Sn (233°), Sb (631°), Te (450°), Au (1064°), Tl (290°), Pb (327°), Bi (268°), Cu (1065°), Cd (322°) and I (114°)†.

Let us assume as before that the substance under investigation is composed of complex molecular groups which vary in constitution as the temperature changes. It is a reasonable assumption to make that the process of association modifies to some extent the internal structure of the atom, for otherwise it is difficult to conceive the nature of the process of association.

If the molecules are simple and do not aggregate let the magnetic moment produced by application of the field be δM per molecule, and when there is aggregation let it be δM_p per particle of type p. The specific dia-magnetic susceptibility will be given by

$$\chi_D = \frac{1}{H} \sum_{p=1}^{N} n_p \,.\, \delta M_p \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where n_p is the number of particles of type p in one gramme of the substance and H is the field intensity.

But n_p varies with the temperature. Write $n_p = n_{0p} \,.\, F_p(\vartheta)$. Then

$$\chi_D = \frac{1}{H} \sum_{p=1}^{N} n_{0p} \,.\, \delta M_p \,.\, F_p(\vartheta)$$

and

$$\frac{\partial \chi_D}{\partial \vartheta} = \frac{1}{H} \sum_{p=1}^{N} n_{0p} \,.\, \delta M_p \,.\, \frac{\partial}{\partial \vartheta} (F_p(\vartheta)) \quad \ldots\ldots\ldots\ldots (4).$$

The variation of dia-magnetic susceptibility with the temperature depends upon factors of the type $\frac{\partial}{\partial \vartheta} (F_p(\vartheta))$ and these may be

* *Versl. Kon. Ak. v. Wetensch.*, Amsterdam, XII. 1910, p. 601.

† See also J. J. van Laar, "On the solid state," *loc. cit.* p. 26.

positive or negative, for the aggregate may increase or decrease in complexity with increase of temperature. It appears that the sign of $\frac{\partial \chi}{\partial \vartheta}$ proves little or nothing as to the validity of Curie's two laws, which are probably true for substances built up of simple molecules. And it cannot be said that this variation in sign of $\frac{\partial \chi}{\partial \vartheta}$ indicates that there is no distinction other than that of mere positive and negative number, between the nature of para-magnetism and that of dia-magnetism.

I have to thank Prof. Sir Joseph Thomson for the interest he has shown in this work, also I must express my indebtedness to Prof. W. M. Hicks and Dr N. Bohr for valuable criticism.

Note on the Chromosomes in Oogenesis and Spermatogenesis of the White Butterfly, Pieris brassicae. By L. Doncaster, M.A., King's College.

[*Read* 26 February 1912.]

In a former note in these *Proceedings* (xvi. 1910, p. 44) I described the behaviour of the chromosomes in the spermatocyte divisions of *Abraxas grossulariata*. As had previously been recorded for other Lepidoptera by various observers, no unpaired or unequal heterochromosome was discovered. The division-figures in oogenesis were too small and crowded for accurate observation. Since in this species sex-limited transmission occurs in the female, and since in *Drosophila* and Man, in which sex-limited transmission occurs in the male, unpaired heterochromosomes have been recorded in the spermatogenesis, it seemed possible that such chromosomes might exist in the oogenesis in Lepidoptera. I find that in *Pieris brassicae* the division-figures are larger and clearer, and the results of my investigation are shortly as follows. The oogonial mitoses show 30 chromosomes, of which eight are smaller than the rest, but there is no visible inequality in the members of any pair. In the growth stage of the oocytes the nuclei pass through (1) a stage with fine tightly coiled spireme ("synizesis"), (2) a fine loose spireme or intertwined threads, leading to (3) nuclei with 14 thicker threads arranged meridionally round the nuclear membrane. These threads then contract to (4) 14 short, thick, conspicuously double chromosomes. During all these stages there is a chromatin nucleolus which, at least when the chromosomes are separately visible, is double. It may be regarded as a pair of chromosomes which do not take part in the spireme stage, as has been described in the spermatogenesis of other species of Lepidoptera.

In the spermatogenesis the spermatogonial chromosomes are about 30; I have found no figure in which I can count them accurately. The early spermatocytes go through stages similar to those of the young oocytes, with chromatin threads and nucleolus, but the meridional arrangement of the chromosomes before contraction is less clear, and in the last phase before division the chromosomes are represented by irregular masses under the nuclear membrane, connected by a reticulum. In the first spermatocyte division the equatorial plate contains 15 chromosomes, of which four are usually smaller than the rest, but the difference

in size varies in different cells. In side views of metaphase and early anaphase no unequal division of a chromosome can be detected. The equatorial plates of the second division show 15 chromosomes; usually four are smaller than the remainder, two commonly being conspicuously smaller and often lying side by side. Some figures show only three small ones, and these differences among the equatorial plates of the second division led me to suspect an unequally paired heterochromosome, but I have been unable to substantiate this suspicion. Daughter-plates of the second division are similar to each other. I conclude therefore that in each sex of *Pieris brassicae* there are 15 pairs of chromosomes, one of which pairs takes the form of a "chromatin-nucleolus" during the growth-phase of oocytes and spermatocytes; in the female all are equally paired and there is no sufficient evidence of inequality in the male. No relation can thus be found between the sex-limited transmission of characters in Lepidoptera and the existence of unpaired or unequal heterochromosomes.

(A fuller paper will appear in *The Journal of Genetics.*)

A group of Rhizopods from the Carboniferous Period. By R. C. McLean, B.Sc., London. Botany School Cambridge. (Communicated by Professor Seward.)

[*Read* 26 February 1912.]

The following notes on the various species of some interesting microscopic organisms, which are here referred to the class of the Rhizopoda, are intended simply by way of an introductory account, and are not to be regarded as an attempt at the production of a comprehensive monograph.

In extenuation of such an indulgence in the privilege of a "preliminary account," it may be urged that the group of organisms here described has suffered a neglect wholly unwarranted, when their beauty and complexity of form, no less than their systematic interest, and generally problematic nature, are considered. This neglect is very probably due to the entire lack of any comparative and connected account of them. The original literature which deals even with portions of the group, consists of but a few isolated papers, and although researches have from time to time been made, since the discovery of the organisms forty years ago, no attempt at a comparative survey or correlation of the various species has ever been made.

If therefore these notes should stimulate any interest which would lead to the settlement of the systematic position of the organisms, their purpose will be fulfilled.

In the Lower Coal Measures of the North of England there occur, in some abundance, a number of microscopic bodies showing related features, which are grouped at present into four genera—*Traquairia, Sporocarpon, Zygosporites* and *Oidospora.*

These four genera are particularly common in the Halifax Hard Bed, but specimens have been found in all the other localities productive of coal-balls, including Dulesgate, Oldham, and Shore.

The Burntisland beds in the Lower Carboniferous, have also yielded two species of *Traquairia,* while on the continent, Dr Kubart has recorded, and Mrs Scott confirmed, the occurrence of *Traquairia* at Ostrau and Karwin in Moravia, in Upper Carboniferous beds which are older than the English Coal Measures.

Another organism which will probably have to be classed along with the above is a calcareous Carboniferous form first referred to by Prof. Judd, and named by Williamson *Calcisphaera**.

Regarding the status and affinities of all these structures there has been the greatest diversity of opinion.

* "Organization of Fossil Plants of the Coal-Measures," Pt. x. *Phil. Trans.* 1879.

Carruthers, describing *Traquairia* for the first time, in 1872, placed it unhesitatingly among the Rhizopods, and compared it with some forms figured by Archer* and Cienkowski† in the previous year, although it must be confessed that the resemblance is not startling. The other four genera were all described and figured, along with *Traquairia*, by Prof. Williamson‡ in his ninth, tenth and twelfth memoirs. He, although at first inclined to regard them as conceptacles, or sporangia, latterly considered them definitely established as the megaspores of Lycopodiaceous plants. This latter opinion was based upon frequent association of their remains with those of *Lepidostrobus* and allied cones. Never, except in a single instance, were the supposed megaspores found in undamaged sporangia. In the single instance referred to, a crucial test of their nature, seven individuals of *Zygosporites brevipes* were found in a complete and very thick-walled sporangium. This evidence in favour of regarding them as megaspores would have to be considered conclusive, but for the fact that the sporangium also contains some dirt, a fragment of a hypha and three coprolites as large as any of the *Zygosporites*, obviously not formed *in situ*, and indicating that the entirety of the sporangium is only apparent and confined to the plane of the section. The true megaspores of the fructifications concerned are now well known. They are very similar to those of many modern Lycopodiaceae, and in no way resemble *Traquairia*.

It is unfortunate that rounded cells which are without doubt of fungal nature, have so often been regarded as integral parts of the structures in which they occur, and interpreted as endosporal cells, microspores, and the like, leading to quite erroneous conclusions.

Strasburger§ and Solms-Laubach‖ judged *Traquairia* and *Sporocarpon* to be portions of Rhizocarpean plants, and compared them to the massulae of *Azolla*, an opinion which, even coming from such learned sources, must be regarded as obsolete. Schenk¶ and Zeiller** both copy this opinion in their text books of botany and fossil botany.

This suggestion of a comparison with the massulae of *Azolla* has not proved very fruitful, as there survive at the present day no Hydropterideae which can afford a sound analogy of structure with the fossil organisms. Nor are extinct forms any more enlightening.

* *Q. J. M. S.* 1869–71; *Proc. Irish Academy*, 1873–4.
† *Archiv f. Mik. Anat.* 1865–7; *Bot. Zeitung*, 1865.
‡ *Phil. Trans.* 1877, 1879, 1883. Part II.
§ See Williamson, *Phil. Trans.* 1879, p. 515.
‖ *Fossil Botany*, p. 183.
¶ *Handbuch der Botanik*, Band IV. 1890.
** *Éléments de Palaeobotanique*, p. 130.

Submitted by Williamson to Haeckel, in 1876, the opinion given concerning them was: that no structures comparable to these organisms were known among the Radiolaria. His opinion was delivered before the publication of the *Challenger* Report on the Radiolaria and it is possible that this judgment might have been subsequently revised. At any rate there are many species figured in the above-mentioned work which readily lend themselves to suggestive analogies; an instance of this being the genus *Auloplegma*, which affords a very plausible comparison with the structure of *Traquairia*.

One paramount objection to their Radiolarian nature is, of course, that none of them are siliceous. Their appearance is that of true vegetable remains, although the prevalent darkness of tint suggests chitin rather than cellulose. In a portion of an insect discovered in one slide, where some unquestionable chitin was present, a comparison was possible, and tended to support this view of their nature.

Chitin is a substance not uncommonly found in the tests of Protozoa of various families, but it is noteworthy that it is particularly characteristic of those occurring in fresh, or only slightly brackish waters.

Among the Foraminifera chitin forms the test throughout the Gromideae, and is also frequently the organic basis of the test in the Arenaceous forms. Most interesting however is the change displayed by the shell of the Miliolidae. Brady* says that in brackish water, where the supply of earthy salts in solution is less than in the open sea, the shells of such species as survive become less and less calcareous as the water becomes less saline, until at last a point is reached where the test has become entirely chitinous, and the water entirely fresh. In species from abyssal depths of the ocean the test was found to be siliceous, which indicates an instructive variability within the limits of a single family.

In *Calcisphaera*, we have, however, a foraminate, calcareous form, and this fact of composition may prove to be a valuable link between it and some other group among the Rhizopoda.

Schorlemmer, consulted by Williamson, considered the replacement of silica by calcite to be impossible, unless the actuality of it were certified by convincing morphological evidence. This evidence has been accumulated by Prof. Sollas† and Dr Hinde‡ in regard to sponges occurring in the Silurian, in Cretaceous rocks and in the Carboniferous Limestone of Derbyshire, where the spicules have been dissolved and replaced by $CaCO_3$; amounting to a definite

* *Challenger* Report on the Foraminifera.
† *Q. J. G. S.* vol. LV. 1899.
‡ Catalogue of Fossil Sponges in the British Museum.

proof that such a substitution may take place. Under these circumstances it is necessary to believe that *Calcisphaera* may have been originally siliceous, in which case it stood very near to the Radiolaria. In the calcified condition it is more suggestive of the *Ramulina* group among the Foraminifera.

Carruthers advanced as an objection to his own opinion of the Radiolarian affinities of *Traquairia*, that it did not possess a "central capsule," a constant feature of the true Radiolaria; but Mrs Scott* in her recent valuable account of the same genus, states that every species is now known to possess that structure. The same is true of *Sporocarpon* and of some of the other forms, so that the objection to their Rhizopodean affinities on this score falls to the ground.

To Prof. Dendy, F.R.S.†, belongs the honour of suggesting that all these forms might be placed in a separate, extinct group of the Protozoa, provisionally allied to the Radiolaria; which is the view least open to criticism in the light of present knowledge, and is the one adopted in the present paper.

In passing on to a morphological description of the species, it may be as well to say a few words regarding the characteristics of the group as a whole. These organisms are to be regarded, in the absence of any organ of attachment, or demonstrable parent —whether plant or animal—as individual organisms, either living a free existence in the water, or united into small colonies, in which they are more or less closely adherent to one another. They are all spherical, with the exception of *Sporocarpon tubulatum* and *Zygosporites oblongus*, which are ovoid, and they are characterized by a tendency to the peripheral development of numerous tubular processes, either radially or tangentially.

In some cases these processes, touching one another all over the surface of the sphere, form a compound investment, completely enclosing the simple wall which limits the central cavity. In other cases they are remote one from the other and are connected by a system of tangential tubes. In extreme cases only the tangential tubes appear. These processes communicate with the internal cavity, and appear to provide a means for the extrusion and extension of the protoplasmic labyrinth from within, by way of pores upon their outer surfaces. In size, the forms varied from ·4—·05 mm. in diameter, the descending series being *Traquairia*, *Sporocarpon*, *Zygosporites*, *Oidospora*. Reproduction was accomplished by means of *spores*, formed within large spore mother-cells, which in turn were surrounded by a mass of periplasm‡. No

* *Annals of Botany*, vol. xxv., April 1911.

† During discussion of the above paper, when read at the Linnean Society.

‡ Cienkowski, "Spore Formation in the Radiolaria," *Q. J. M. S.* 1871, vol. xi. N.S.

dimorphism of the spores has yet been observed—the supposed instances of it noticed by Williamson being due to a postmortem development of fungal spores in the central cavity. It is just possible that certain commonly occurring small spores, of a dark colour, may represent microspores, but they are more probably only fungal, judging, that is, by their mode of occurrence.

Young phases have not been discovered, possibly owing to their fragile nature, or to minute size. What slight indications of the development have been observed denote that the spines, where they occur, are produced by the centrifugal elongation of small peripheral chambers, originally contiguous, which become separated by the continued growth of the sphere wall.

That the structure was in all cases unicellular, and comparable with that of the Protozoa, seems evident, as no segmentation of the organism occurs except during sporulation.

It has been stated above that no organ of attachment has been discovered in any one of the very numerous specimens extant, and having in consideration their small size, and the large portion of each individual included in a fossil section of average thickness, this constitutes a conclusive argument against the existence of any such appendage. If the hypothesis that the numerous superficial pores served the purpose of foramina for the extrusion of a protoplasmic labyrinth be well founded, it naturally follows that the mode of nutrition would probably agree with that of similar, recent forms of Rhizopods, in which bacteria and small algae are caught, enveloped and digested in the meshes of the outstretched network, without ever being ingested in the main central mass of the animal.

Under these circumstances an operculum or other large orifice in the test is needless, in so far as nutrition is concerned; although in some modern forms it does occur.

Mrs Scott has figured, from slide W. 1077 of the Williamson Collection a structure which she believes to be such an operculum. After a careful search over the section in question nothing appeared which lent itself strongly to the support of such an interpretation. It is not to be denied, however, that such orifices may exist.

Before proceeding to describe the species of the group distinctly and in detail, it is worth remarking that if any modern forms can be found with which these organisms might be correlated, valuable evidence in regard to the conditions, whether fresh, salt, or estuarine, under which the coal beds were laid down, and of the topography of the coal measures would result. Carruthers originally suggested that they might form indicators of oscillations in level during deposition.

To summarise the general conclusions regarding the group in a few words, we may say that we are dealing with a close group,

the species of which show clearly marked inter-relationships, but that the group as a whole exhibits no intimate affinities with any living group.

The Radiolaria may be indicated as the nearest Protozoa which approach them, and among these the small recent group of the Aulosphaerida (Röhren-Kugel Radiolarien)*, on account of their hollowed echinate spines and ramifying tangential tubules, are the most likely parallel. Indeed all the Phaeodaria present a greater or lesser degree of analogy with these organisms. Although debarred by their physical constitution from a place within the group Radiolaria, they may yet be classed as a second, distinct division of Rhizopoda Radiaria, subsidiary to the great division named above.

Rhizopoda Radiaria.

Family. Traquairidae. Extinct Protozoa, typically spherical and radially symmetrical, secreting a chitinous test of complex structure, which is composed either of elongate radial processes, tangential tubuli or a lobate stereome. Reproduction by means of spores produced from large mother-cells, which fill, and are enclosed within, a thin-walled central capsule.

Within the Traquairidae, *Traquairia* is the oldest established genus.

Traquairia. (Carruthers—*Report of Bot. Section. Brit. Ass.* 1872) was compared by its discoverer to the Xanthidia in flints, and to some Rhizopods described by Archer† and by Cienkowski†.

This genus has been recently the subject of investigation at the hands of Mrs Scott. In looking over the Scott Collection, during the process of cataloguing, she came to distinguish four species which she has named and described.

The first of these, which is also the commonest, is named in honour of the discoverer of the organism.

T. Carruthersii.

This is the original form which Carruthers himself described.

The radial processes, as in all the species of *Traquairia*, take the form of elongated spines. These occur distributed pretty evenly over the entire surface of the sphere, and not grouped in any way. They are stout and broad at the base, the greater portion of the circumference of the spine at this point being occupied by the openings of the large tangential tubuli, which form a stout network of short tubes all over the exterior surface. These tubuli are not confined to one plane, but are frequently intertwined, passing one beneath another.

* Haeckel, *Die Radiolarien.*
† *Loc. cit.*

The spines taper slightly, are equal to about one half the diameter of the sphere in length, and commonly branch at the extremities. They increased in thickness and strength with age, so that they must perforce have contained living protoplasmic material.

They open into the interior cavity by means of a large proximal pore, and bear hollow echinations in whorls of 10—16 along their entire length. These echinations are produced into a complex system of branching and anastomosing fibrils which form a dense mass near the base of the spines, and become less and less conspicuous towards the top, the extreme tip bearing only inconsiderable tufts.

The whole mass thus presents a conical appearance, the spine itself forming the axis. Fibrils—or *ramalia* as they may distinctively be named—of adjacent spines do not connect with each other in any way. The spines were not brittle when young and are often abruptly flexed. Old spines were however less flexile.

The bases of the spines contain a delicate lining membrane, apparently forming an internal vesicle.

The tangential tubuli do not bear any ramalia. This is a specific feature, as will be seen further on.

Inside this complicated test is found the delicate *sphere wall*, perforated only at the base of each spine, which forms a coat inside of the peripheral network of tubuli. Within this again is produced the "central capsule" which has been the ground for previous comparisons of the genus with the Radiolaria.

The wall of the central capsule is thin and smooth, and during life must have been formed close beneath the sphere wall. In this position it is commonly preserved. This central capsule contains, in favourable states of preservation, a large number of thin walled vesicles, apparently embedded in a mass of mucilaginous material, which may be termed *periplasm*, though whether it really represents such a substance, or merely mucilage is undetermined.

In several instances small objects have been found within these vesicles, which have all the appearance of having been formed there, and from their structure and lack of exterior origin or attachment may be conceived to be the true spores of the organism, the larger vesicles being interpreted as mother-cells. They are referred to hereinafter as *sporoids*. The spores consist of a single comparatively large central cell, surrounded by a layer of very small vesicles, which are rounded, almost hemispherical, although they touch each other tangentially, all over the surface of the central cell, thus recalling the *Oidospora* about to be described.

No developmental phases have yet been obtained, and the origin of the spines and tubular network from contiguous vesicles by radial and tangential elongation respectively can only be surmised.

In general appearance *T. Carruthersii* is much lighter in colour than the species next to be described, being quite a pale-brown and of a furry appearance, owing to the extensive development of the fine ramalia.

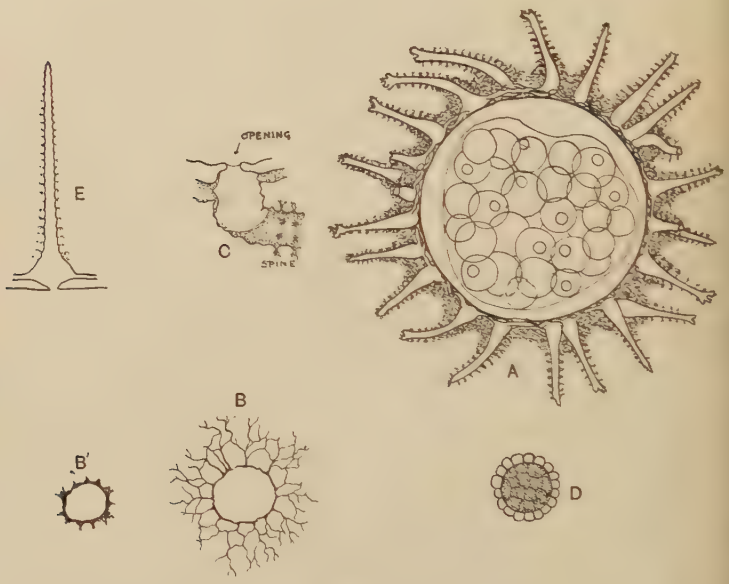


Fig. 1.

A. Diagrammatic view of a transverse section of *Traquairia Carruthersii*, showing the central capsule containing sporoid cells and small spores.

B, B′. Transverse sections through a spine of *T. Carruthersii*, taken respectively near the base, and near the apex; showing the decrease in the development of the ramalia.

C. The basal portion of a much-flexed spine of *T. Carruthersii*, showing the proximal opening into the central cavity of the organism.

D. Enlarged view of one of the small spores in the above species.

E. Diagram of spine construction in *Traquairia Spenceri*.

T. Spenceri.

This occurs like the above in the Halifax Hard Bed, but a single specimen, in the Williamson Collection, is recorded from Oldham.

The spines are very much longer than in *Carruthersii*, being not infrequently almost as long as the diameter of the sphere, but

hey are less numerous. They taper to a point and do not branch, hile they are evenly arranged over the entire surface as in *. Carruthersii.* The bases are swollen into bulbs, and the evelopment of the fine ramalia is quite sparse, so that the spines ppear as if naked. Here, as in *Carruthersii*, the spines were very exile, and, Mrs Scott says, were frequently bent into hook-like orms. The circumferential network consists of a very regular ystem of comparatively narrow tubuli, which unite the spines one vith another. Instead of passing one over another, the tubuli in his case form junctions among themselves so that they present system of nodes and internodes. No ramalia are produced on hem.

The capsule is similar to that in *Carruthersii*; but the small pores have not been observed. The secondary "inner capsule" ometimes observed is certainly in some cases the appearance presented by the existence of a large interior bubble in the matrix. Mrs Scott has figured a structure in the capsule of this species vhich may be an operculum. The general colour is dark, almost opaque. *Spenceri* is much less common than *Carruthersii.*

These two species are not nearly so sharply defined as are the pecies of *Sporocarpon*, and intermediate forms are not uncommon. As typically developed, however, they are certainly distinct, and nay be with advantage considered as being separate species.

T. burntislandica.

In this species we have a thoroughly different type. Although described from the Burntisland beds, of Lower Carboniferous age, it appears to have survived into the Upper Carboniferous, specimens almost, if not absolutely, identical being found in the Lancashire coal-balls. It may be considered as the oldest species of the genus.

The spines are large, thick walled and sparse: they do not taper, neither is there any proximal expansion. They are often broken in pieces and appear to have been brittle. The echinations are very large, and arranged in several regular longitudinal series or orthostichies, giving the spine in longitudinal section a moniliform appearance. They bear very coarse, tubular ramalia which are not branched beyond the third degree, and whose ends are open. These tubular ramalia proceed outwards a regular, though short, distance from each spine before branching, which then takes place profusely. In this way is formed a cylindrical outer coating of tubuli, separated by a space from the spine which it surrounds. The network between the spines is very open, and is formed by tangential tubuli which proceed in a radiating manner from the base of each spine, interlacing with each other, but remaining distinct from the tubuli which proceed from the other neighbouring spines. They are themselves branched, forming by their branching

tubuli, which are indistinguishable from the ramalia borne by the spines.

The sphere wall is attached to the base of each spine, and forms a continuous coat, underneath the tubular test.

The capsule and sporoid cells are similar to those of the above species. Owing to the loose structure of the test, fungus spores are more commonly found in this than in the other species.

T. Ramex. (Latin—*Ramex*, a pectoral bloodvessel. In allusion to the tubular, branching ramalia.)

This is a new species, which it is proposed to separate from *T. burntislandica* on the ground of several important differences. It comes from the Halifax Bed, and is similar to *burntislandica* in general type. The spines however are very few, and are either solitary or in small groups. They are brittle, taper to a point, and are constricted just above the base. They are shorter than in *burntislandica* and the ramalia do not form a continuous investment around them, but branch only slightly, and that close to the spine. The tubular network is similar, and also bears ramalia plentifully.

Most important, however, in distinguishing this species is the absence of any sphere wall, the tubuli forming the only structural investment of the organism.

Capsule and sporoids are of the normal description.

T. stellata.

This is by far the rarest of the species, and I have had no opportunity of examining any specimen. It is described and figured by Mrs Scott* as possessing instead of tubular spines, a species of lobed wall, the lobes being very long radially and segmented by transverse and periclinal divisions. These lobes bear ramalia, so that notwithstanding a superficial resemblance to *Sporocarpon asteroides*, it must be classed within this genus. A central capsule is present. Like *burntislandica* this species comes from the Burntisland beds. It is therefore an older form than most of the other species.

We now pass to the second, the largest genus of the Traquairidae namely *Sporocarpon*. In this genus some six very well defined species are included, although it is very difficult to frame any definition which would cover all, save in the most general and unlimited terms.

The species which is usually taken as the type is one of a very striking nature, namely *Sporocarpon elegans.*

S. elegans.

The wall in the usual weathered state of preservation appears to be made up of hour-glass shaped cells, touching at the upper

* *Loc. cit.*

and lower bulb, and having spaces between the constricted "waists" or median portions. These hour-glasses are usually widely open to the exterior, but some appear to be produced into long tapering spines. There can be no doubt, however, that all the cells were

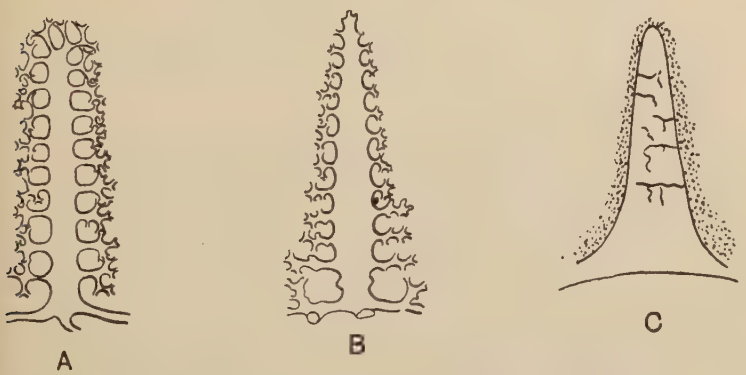


Fig. 2. Scheme of Spine forms in three species of *Traquairia*.

A. *Traquairia burntislandica.*
B. *Traquairia Ramex* (sp. nov.).
C. *Traquairia stellata* (after Mrs Scott).

originally so produced, but that through the fragile nature of the spines, they have been reduced to a common level by weathering. The structure thus represents a wall formed of tapered spines, swollen and contiguous towards the inner extremities, and below this swelling tapered to a fine tube which again expands into a second series of contiguous bulbs, abutting on the central cavity of the organism. These spines are smooth, and may be single pointed, bifid or trifid, as in *T. Carruthersii.* The median lumen is continued centripetally and opens into the central cavity. It is not decided whether the tips of the spines are pierced by pores, or not.

Between the concentric coats, formed by the two series of swellings, there is a space, traversed radially by the numerous fine "waists" of the hour-glass portions of the spines. Williamson declared, on the basis of some tangential sections of *elegans* in which walls appeared in this space, that it was filled by a soft tissue, formed of triangular cells, whose angles were the "waists" and whose walls divided the space between into regularly arranged elements.

It is clear in other preparations, however, that these supposed walls are indeed tubules, forming a tangential network joining up adjacent spines comparable to that in *Traquairia.*

On morphological grounds it is in any case difficult to see how a cellular tissue could arise in a space which is in truth exterior to the organism, although enclosed in the structure of the wall.

Throughout all the species, so far as observations extend, the central cavity presents exactly the same features as in *Traquairia*. It is therefore unnecessary to reiterate the characters for each individual species. Williamson found 45 *elegans* in a single cone of *Lepidostrobus*, which gives some index of its abundance in the coal-balls.

S. compactum.

The wall is formed by a smooth, thin, imperforate membrane. This is the only case where no perforation of the sphere wall has been seen, but comment will be made on this seeming anomaly later on. Upon the outside of this membrane is an attached wall formed of a palisade layer of peripheral "vesicles"—so to call them—small bladder-like cells, longer than their breadth, flattened against the membrane wall at the base, and sharply tapered to a mucronate point. The exposed surface of these vesicles is covered with very minute echinations, which bear tiny tufts of hair, analogous,we may suppose, to the ramalia in *Traquairia*. The vesicles themselves are lined with a delicate membrane. It was originally suggested* that *compactum* was merely a growth phase of *elegans*, this view being based upon specimens in which the vesicles of *compactum* were becoming elongated into spines strongly resembling those of the other species.

This view is incorrect. The spines of *compactum*, which are produced by a proportion only of the vesicles, are the adult stage of that species, and are very different in character from the spines of *elegans*, being covered with the minute tufts of papillae spoken of in connection with the young vesicles. They are moreover not nearly so acute as in *elegans*. The young phase of *elegans* is not known, but it is presumed that the adult structure must have been arrived at by the centrifugal elongation of a layer of prismatic vesicles in a similar way to that described in the present species. The vesicles of *compactum* never become separated from one another.

In regard to the perforation of the sphere wall in this species, it may be remarked, that in some species of *Traquairia* this perforation occurs only beneath the spine insertions, so that we may expect something of the same sort to be found here. No section passing through the proximal end of a fully developed spine is, however, as yet available. As *compactum* is the commonest species of *Sporocarpon*, such a specimen will no doubt be discovered ere long.

* Williamson, "Organization of Fossil Plants of Coal-Measures," Pt. x. *Phil. Trans.* 1879.

S. tubulatum.

A species similar to the last, classed by Williamson as *compactum var. tubulatum.* There seems little doubt that it really forms a distinct species, as it has several characters peculiar to itself. In the first place it is not spherical, but ovoid, one diameter being about $\frac{1}{7}$ greater than the other. This feature is shared by one other form only, within the Traquairidae, namely, *Zygosporites oblongus.* The specimen figured by Williamson was a young phase—corresponding to the young phase of *compactum*—that is to say the state previous to the development of the spines. In this condition the peripheral vesicles form a compact wall, being smaller at their proximal ends and enlarged towards the exterior. The extremities are not mucronate as in *compactum*, but rounded smoothly off. Later on, these vesicles become centrifugally produced to form spines somewhat resembling those of *elegans*, that is to say, at the point where the original termination of the vesicle was, in the young state, they develop a globose swelling, below which a slight constriction becomes evident. The upper portion of the spines, above the swelling, tapers smoothly to a solid point. A noteworthy difference between this species and *compactum* is found in the fact that all the vesicles become produced into spines, as in *elegans.* In this way, the originally contiguous vesicles become separated one from another, being thrust apart by the development of the swellings. If the spines then get weathered away, their lower portions not being supported by any tangential tubuli, fall together and become disorganised. Proximally, each opens into the interior cavity of the organism by a large pore, to

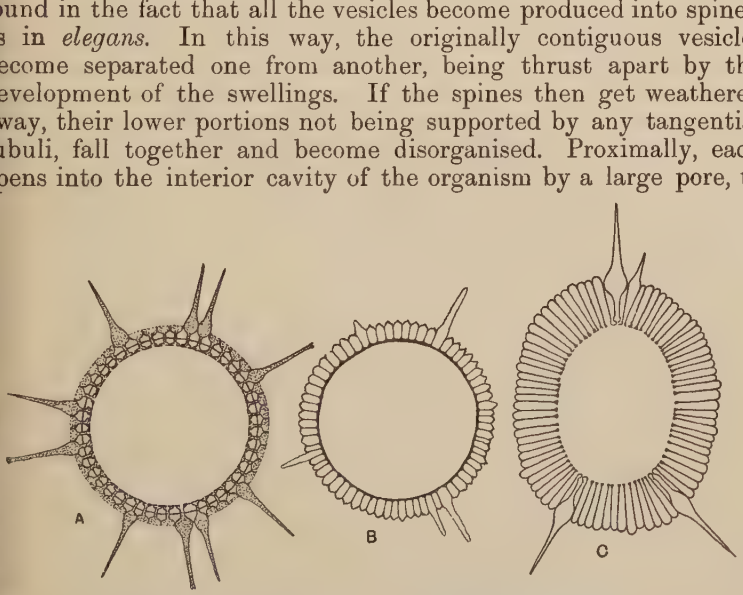


Fig. 3. The original types of the genus *Sporocarpon.*

A. *Sporocarpon elegans.* B. *Sporocarpon compactum.*

C. *Sporocarpon tabulatum.* All three showing some completely developed spines.

The central capsule and its contents in all these species are quite similar to that in *Traquairia Carruthersii*, and are therefore left unrepresented.

which it is connected by a constriction. There are no exterior papillae on the surface of the spines.

This species is very uncommon. No capsule or sporoids have yet been observed.

We now pass to a second type of *Sporocarpon*, which shows such remarkable differences that it is difficult to regard it as satisfactorily included in the same genus as the species described above.

The first species, one which shows an intermediate form of structure, is that described by Williamson in his ninth memoir* as *Sporocarpon cellulosum.*

S. cellulosum.

Here we have again the typical spherical form, bounded by a rather stout sphere-wall. Outside this is a curious compound wall, the true nature of which remains in some doubt. It appears to consist of short, stout, tubular processes, which occur in some places bunched together into radiating groups, but are, as a whole, distributed fairly evenly over the entire surface. Those forming the groups are considerably longer than those occurring separately, thus giving the test, in radial section, a lobate appearance. These tubes are quite open at the extremity, and are connected together by parallel series of fine tangential fibrils, running straight from one tube to another, the tubes themselves being divided horizontally by similar fibrils. Whether these are truly fibrils or represent the edge-view of fine plates, remains doubtful, although the latter alternative is, on comparative grounds, a possible one. Well-preserved specimens are not sufficiently common to decide the question. Nor have proximal openings to the tubes been discovered in any extant example. The tangential connections give the whole test, viewed under a low power, something of the appearance of corky tissue, a resemblance which presumably suggested the specific name.

All appearance of the tubes becoming produced into spines is absent, nor is it to be regarded as a probable contingency that they did so develop.

What imperfect remains of the central capsule and sporoids have been preserved, are sufficient to certify that they followed the normal type.

S. asteroides.

This is a commoner species than the last, and is a striking development of a novel order of structure, the divergence from the *elegans*-type being very strongly marked.

The test consists of the usual smooth inner wall, which is surrounded by a thick mass of apparently parenchymatous tissue. This tissue is composed of rounded elements, quite undifferentiated and resembling pith cells in appearance. No cuticularization a

* *Loc. cit.*

the exterior surface is evident. It would bring *asteroides* more into line with the rest of the group, could it be shown that this supposed parenchyma was in reality only the appearance presented by a mass of anastomosing fibrils. There is nothing in the existing specimens to render such a view untenable, but direct proof of its truth is wanting. The specific name is derived from the fact that this tissue is produced radially into long lobes, thus giving the radial section an asteriated outline. Capsule and sporoids are typically developed.

The last species of *Sporocarpon* is *S. pachyderma.*

S. pachyderma.

In this form the test consists of an interwoven mass of large tubuli, an investment which may reach a thickness as great as the diameter of the central cavity. These tubuli branch and anastomose very freely, the result being a dense tissue, which envelopes the organism. On the outer surface, openings are provided by short branches, which pass outwards, and open freely to the exterior. The tubuli are large and smooth, their walls are thin, and the internal lumen comparatively wide. There is no indication of radial development, save in one anomalous specimen, which remains unexplained, wherein is found a ring of large, stout, radial tubuli, developed on the *interior* surface, that is to say centripetally, thus diminishing the size of the internal cavity. This compact palisade-layer is formed by the ingrowth of the terminations of investing tubuli. It is filled towards the interior by very dark granular contents, and may represent a senile phase of radial development, comparable to that in *S. compactum,* or *tubulatum.* The sporulation is typical and does not seem to be connected with this unexplained centripetal growth. A second form of *pachyderma* occurs, in which the investment of tubuli is much looser, the interstices being occupied by connecting fibrils.

From the above account it will easily be perceived that the divergence between the type of the first three species—which we may call the "*elegans*-type"—and that of the last three, or the "*pachyderma*-type," is very considerable, and hardly compatible with their inclusion under the same generic title. Acting on this consideration, it is perhaps not too much to suggest that the three species *cellulosum, asteroides* and *pachyderma* be provisionally separated from *Sporocarpon* under the generic title of *Perichoderma.*

To justify such a division it must be recognised that each "genus," *Sporocarpon* and *Perichoderma* really stands for a family, or group of genera, whose species it is impossible to separate in fossil forms. At the same time each "species" may be safely considered as containing not more than one actual genus, because

in these minute creatures small differences of form are more conspicuous and easily recognisable than in higher organisms, known only in isolated sections, and in consequence, genera become distinguishable without difficulty. Even if the separation of *Perichoderma* from *Sporocarpon* be adopted, the three forms remaining in each genus show greater divergences than would be compatible with inclusion within a single genus of recent Rhizopods, but to pursue the subdivision to its logical extreme would, apart from its impossibility, be utterly inconvenient and without any compensating theoretical value.

The separation of *Perichoderma* serves to segregate two groups of forms which do show strongly marked differences of character, without incurring the confusion of a needless multiplication of names.

The "*elegans*-type" has the priority in the genus *Sporocarpon*, therefore it is that the "*pachyderma*-type" receives the new name.

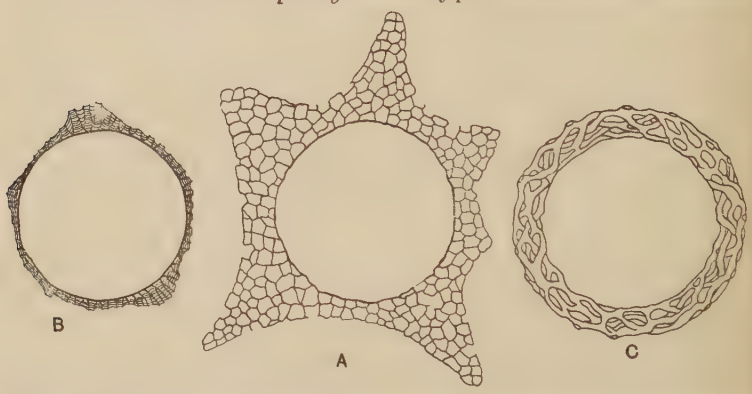


Fig. 4. The three species which it is proposed to separate from *Sporocarpon*.
A. *Perichoderma* (*Sporocarpon*) *asteroides*. B. *Perichoderma cellulosum*.
C. *Perichoderma pachyderma*. The investment of tubuli is commonly much thicker than is represented in the figure.

Two objects which Williamson described as belonging to *Sporocarpon*, under the respective names of *Sporocarpon ornatum* and *S. anomalum*, are now known to be transverse sections of Pteridospermic seeds, the first, *ornatum*, representing *Physostoma elegans*, and *anomalum* some other, not precisely ascertained.

The third genus of the group—*Zygosporites*—is much smaller, both in number of species and dimensions than either of the preceding genera, and it is at the same time of a more dubious character.

These organisms have been claimed at various times to represent the megaspores of some vascular cryptogam, the zygospores of Zygomycetes, and the zygotes of Desmids.

Regarding the first alternative it is sufficient to refer to the remarks at the commencement of this paper, and to Mrs Scott's paper on *Traquairia** wherein were advanced arguments against such a conclusion.

The second is a more plausible alternative. Van Tieghem describes† the formation of the zygospores in *Phycomyces nitens* which show very distinct points of analogy with *Zygosporites brevipes*. Indeed there can be no doubt that such structures do occur in the coal-balls, and that in no small number. Excellent specimens have been found in which the suspensory hyphae are still obviously attached to the zygospore. It is unfortunate that these should be of such a similar character to true *Zygosporites*, for they are very easily confused with them. At the same time, although superficially similar, they are distinguishable under a critical examination, and it may still be maintained that there exists a true individual organism, corresponding to the type of *Zygosporites* which is never found in attachment, and which is separable from all similar reproductive organs of cryptogamic plants. In regard to the third suggestion of their nature—that they are the zygotes of Desmids, it may suffice to say that there is no reason why the resistant membranes of the parent plants, which must have been very numerous, should not also be found. No such discovery has ever been reported from these rocks.

Of true *Zygosporites* there are found three main types with minor forms, differing in greater or less degree from the type, which can hardly be considered as distinct species.

Zygosporites brevipes.

Here we are dealing with an obviously unicellular structure, for the entire organism consists of a single spherical cell, enclosed in a smooth wall, there being no outer test, except a pellucid outer membrane which may be the analogue of the structure that becomes elaborated into the highly complex outer wall in the preceding genus.

The sphere wall in *Z. brevipes* is produced into a number of short hollow spines, the lumen of which is freely confluent with the central cavity of the sphere. These spines taper towards their outer extremities, and terminate in a tuft of tiny branches which are hollow and open to the exterior. This open character at once distinguishes them from zygospores, in which the radial outgrowths consist of solid ramenta, formed from the spore wall and containing no permanent lumen, comparable indeed, to the episporic outgrowths found upon the megaspores of some Lepidodendra. In *Zygosporites* the spine walls are in no way differentiated from the sphere wall: both are smooth and of an equal thinness. The spines

* *Annals of Botany*, vol. xxv. April, 1911.
† *Annales des Sciences Naturelles*, Sèr. v. Tom. 17.

are not more than $\frac{1}{4}$—$\frac{1}{3}$ of the sphere-diameter in length, and quite stiff. They project through the outer pellucid layer, which is frequently weathered off.

Zygosporites brevipes is very plentiful indeed, and a large percentage of fossil sections show one or more specimens of it. It is not uncommonly found in groups of 3—6. There occur several varieties of the type, which are of greater or less size as the case may be, differing also in the number and thickness of the spines.

One variety, which shows a longer spine than the ordinary, while distinguished from the next species by the greater size of the sphere, was humorously named by Williamson *Zygosporites brevipes, var. longipes.* There exists also a variety in which the spines do not branch, but taper to a sharp point. A thin membrane lining the interior cavity, and faint remains of sporoids have been detected in a few instances.

Z. longipes.

This is distinguished from the preceding form by its much smaller size, and the great development of the arms. In *Z. brevipes* the spines are mere appendages of the sphere, while here, the sphere becomes subsidiary to the spines, whose bases cover such a large area that they give the central body, in transverse section, quite a polygonal outline. These long arms branch at their extremities in exactly the same way as in *Z. brevipes*, but they are much thinner in proportion to their length than in that species. No capsule or other contents have been seen. This species is much less common than the above. Although suspiciously like a zygospore in appearance, it has never been found with any organ of attachment, and as a fairly thick fossil section includes the whole organism, there would seem no reason why such an organ should not be discoverable, if present.

Z. oblongus.

Here is a striking departure from the spherical form so common in the rest of the group; *Z. oblongus* being, as its name implies, elongate in shape, forming a cylinder with rounded ends, rather like a short thick sausage. The wall is smooth and dark brown, as in the other species, and the radial processes (they can hardly be called spines) evenly distributed all over. They are very short indeed, and broad, being little more than triangular punctures in the wall with outwardly turned edges. Sometimes they may divide into two or three segments but do not branch in any decided way. (In transverse section they give to the outline of the organism something of a castellated appearance.) No attachment has been found.

One example has shown some disorganised contents, but no regular capsule is preserved.

We now pass on to the last genus which undoubtedly falls within this group. The genus *Oidospora*, founded by Williamson, in company with *Sporocarpon* and *Zygosporites*, contains only one species. It is by far the smallest of any of the organisms previously described, being only about ·05 mm. in diameter. Only three slides have been available. Two are in the Williamson Collection in the British Museum, in one of which it occurs in extraordinary abundance, and the third is in the University College Collection in London.

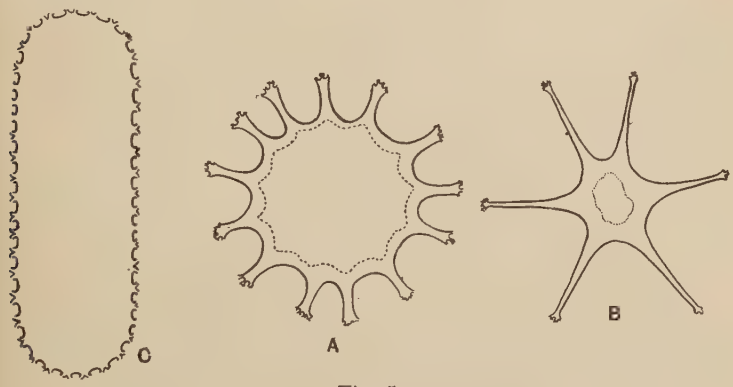


Fig. 5.

A. *Zygosporites brevipes.* Internal membrane dotted.
B. *Zygosporites longipes.*
C. *Zygosporites oblongus.* Longitudinal section.

Oidospora anomala.

A minute form recalling several species of *Sporocarpon*, with which, but for the difference of size, it would naturally be classed. It consists of a central cell, which is bounded by a single layer of large contiguous vesicles about equal in length to the diameter of the sphere and very much rounded off at their outer extremities. There is no sign of any perforation between central cavity and exterior vesicles, the division being effected by a thin wall. No contents have been discovered in the vesicles, and only faint traces of membrane in the central cavity exist to represent the capsular contents.

In the University College specimen, two appear to have grown together, but this is unique among the extant examples. Decidedly the organism was gregarious, to judge from the numbers discovered in Williamson's slides, although the colonies seem to have been few and far between.

It is just possible to refer briefly to the fifth genus, investigations upon which will be published later. This is a form described also by Williamson under the name of *Calcisphaera*, from

a Carboniferous limestone, sent to him by Mr Siddall of Chester. It occurs in vast numbers in this limestone, which comes from Rhydymwyn near Mold in N. Wales, and, distinctively from its allied genera, is calcified. Whether this calcification be original and vital, or secondary in origin remains to be seen. There are many species, all characterised by the same radial symmetry and

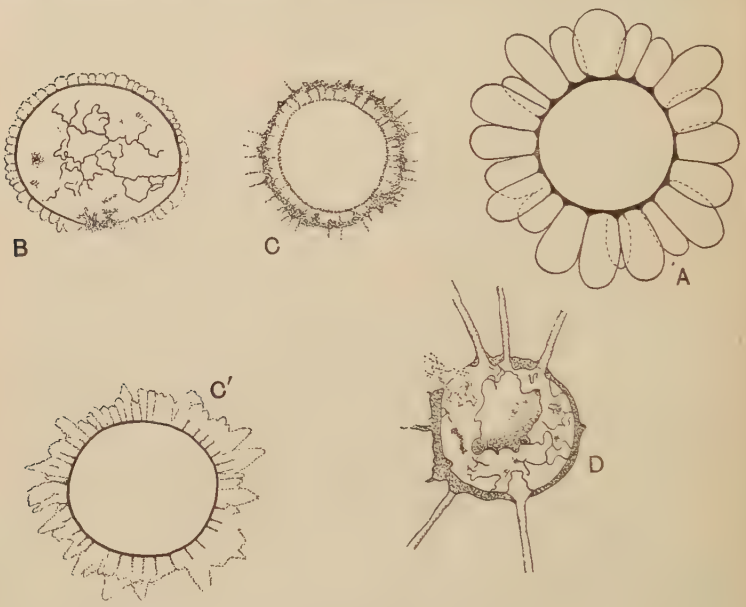


Fig. 6.

A. Section of *Oidospora anomala*. B. *Calcisphaera cancellata*.
C, C′. *Calcisphaera fimbriata*? D. *Calcisphaera spinosa*.

the fenestrated or perforated test which is so constant a feature throughout the group here described. Similar forms also come from the Devonian Corniferous limestone of Kelly's Island, U.S.A.

To the kindness of Mr J. D. Siddall, I am indebted for the loan of his original preparations of *Calcisphaera*, work on which may bring to light some features of interest, in comparison with the Foraminifera and the Radiolaria.

Figure 6 above shows one or two forms sketched from these preparations, showing the imperfect nature of their preservation, and the similarity of the general form to that prevailing among the Traquairidae. This imperfection of outline strongly suggests that replacement of the original substance by secondary calcite has taken place. Sollas* records that in sponge-spicules which have

* *Q. J. G. S.* vol. LV. 1899.

been secondarily altered into calcite, the whole outline becomes indistinct, as in this case.

It is noticeable that some species of *Calcisphaera* have left carbonaceous remains (*C* and *D*, fig. 6) which suggests that they too may have been chitinous in life.

This leads us to an interesting speculation regarding the origin of the group. Dixon and Vaughan* have shown that the Radiolarian-chert, and *Modiola* phases of the Lower Carboniferous succession of South Wales, in which *Calcisphaera* also occurs, are to be regarded as deposited in large coastal lagoons, kept from undue concentration in the sun's heat, by the access of fresh land-water.

Now Radiolaria do occur in such situations, as is evidenced in the account of a littoral plant deposit of Gondwana age, given by Dr Coomáraswámy†, in which deposit Radiolaria occur among the plant impressions, in a fine-grained and thin-bedded mudstone. If therefore *Calcisphaera* were originally siliceous, before the replacement of the silica by calcite, it may well have been a development from true Radiolaria becoming adapted to brackish waters.

If the example of the Miliolidae be of any weight, a decrease in the freshness of these littoral waters might lead to the partial adoption of a chitinous structure, as evidenced in the carbonaceous nature of some *Calcisphaera* remains, finally resulting in a completely chitinous habit, and complete adaptation to the fresh land-waters.

The existence of the other Traquairidae in the coal-balls of the Upper Carboniferous, seems to indicate that these chitinous forms attained their hemera in the vast swamps of the Coal Measures, and died out when these passed away.

Although much of the above is purely suppositious, yet it is at least coherent, and conformable to the existing state of knowledge. For this reason it is tentatively advanced; merely as a possible suggestion, for further investigations to confirm or disprove.

In conclusion I wish to express my indebtedness to Profs. F. W. Oliver and A. C. Seward, and to Profs. Garwood and McKenny Hughes, for their interest and assistance, in the furtherance of work upon these organisms. To Dr Bather of the British Museum, S. Kensington, I am also under obligations for permission to examine and photograph specimens in the Williamson Collection.

* "On the Carboniferous succession in Gower," *Q. J. G. S.* Nov. 1911.

† *Geo. Magazine*, 1902, p. 306.

The Quantities of Radium and Thorium Emanations contained in the Air of certain Soils. By JOHN SATTERLY, D.Sc. (Lond.), M.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 11 March 1912.]

IN a previous paper* the author described some experiments made to measure the amount of radium emanation in the air of soils. The air is abstracted by means of an aspirator and a narrow pipe let down into the soil. When sufficient air has been collected it is passed into a testing vessel and the radium emanation estimated from the electrical leak produced. Detailed work was carried out with four pipes, three of them—those at the Cherryhinton Chalk Pit, the Observatory drive, and in a lawn in the town of Cambridge—going to a depth of 106 cms., and the fourth—that in the court adjoining the Cavendish Laboratory—going down 152 cms.

The experiments have now been carried on throughout a whole year, and the results are given in Table I. The monthly means are given for each pipe. For the first three pipes about three or four readings were taken each month during the first six months and only one a month during the rest of the year. The Cavendish pipe averaged about ten readings a month, except for Sept., Dec., Jan., Feb., when only about three readings a month were taken.

The numbers quoted are the leaks (in cms. of the electrometer scale per minute) produced by the emanation contained in 3 litres of soil-air, all being reduced to a common sensitiveness of the electrometer.

Previous experiments† have shown that a leak of 1 cm. per minute would be produced by the amount of emanation in equilibrium with 13×10^{-12} gm. of radium. It is therefore an easy matter to convert the last three lines of the table into the emanation content expressed in curies, the curie being that amount of emanation which is in equilibrium with 1 gm. of radium.

The results are shown in the following Tables.

* *Proc. Camb. Phil. Soc.* vol. XVI.
† *Ibid.* vol. XV.

TABLE I.

1911 and 1912	Chalk Pit at Cherryhinton, near Cambridge	Shrubbery of Drive leading up to the University Observatory, Cambridge	Lawn at 104, Mawson Road in the town of Cambridge	Lawn in court adjoining the Cavendish Laboratory, New Museums, Cambridge
March	11	49	50	30
April	19	—	14	24
May	—	43	13	52
June	19	41	83	44
July	—	34	67	69
Aug.	9	28	59	52
Sept.	12	53	63	30
Oct.	21	64	76	32
Nov.	14	78	94	27
Dec.	21	67	59	19
Jan.	—	—	—	30
Feb.	27	51	18	35
Mean	17	51	54	37
Highest single reading	27 (Feb.)	78 (Nov.)	94 (Nov.)	78 (July)
Lowest single reading	7 (May)	25 (June)	13 (May)	9 (Nov.)

TABLE II.

Amount of Radium Emanation per litre of soil-air.
Emanation expressed in curies $\times 10^{-12}$.

	Chalk Pit	Observatory Grounds	Lawn in Cambridge	Lawn adjoining the Laboratory
Mean for the year	74	220	230	160
Highest single reading...	120	340	410	340
Lowest single reading ...	30	110	57	40

The average of the means for the year of the last three columns is 200, i.e. the emanation content of soil-air is 200×10^{-12} curie per litre of air. In comparison with this Prof. Joly* gets about 200×10^{-12} for the air from about 100 cms. down in the Park of Trinity College, Dublin (calcareous soil), and Mr Sanderson† gets 240×10^{-12} for the air from about 120 cms. down under the basement of the Sloane Physical Laboratory at Newhaven, U.S.A. (soil of disintegrated sandstone). The average value of the emanation content of atmospheric air is about $0{\cdot}1 \times 10^{-12}$ curie per litre, so that soil-air is about 2000 times as rich in radium emanation as atmospheric air.

It will be noticed that there are great fluctuations in the amounts of emanation obtained from the same pipe at different times. The search for a correlation between these and weather fluctuation has been described in the previous paper. The only pipe which gave any correlation was that in the court adjoining the Laboratory; it always gave low results after rain and high results in fine weather. The readings from this pipe in January when the ground was covered with 10 cms. of snow, and also during the severe frost of Jan. 28—Feb. 6 were not abnormal.

It remains now to connect the emanation content of soil-air with the radium content of the soil. To do this it is necessary (1) to know the relative volumes of air and soil in order to find what weight of soil is associated with a given volume of air, and (2) to know the relative weights of dry soil and water in the naturally occurring damp soil.

The experiments made to determine these factors are of necessity only very approximate. A cylindrical earthenware pot of capacity 800 c.c. was used to hold the earth, and a tall glass cylinder of 2 litres capacity was used as a mixing vessel. A litre of water was poured into the latter and the height of the water marked with stamp paper. A further 800 c.c. water was then added and the height again marked. The cylinder was now emptied down to the litre mark. The earthenware pot was now filled with soil level with the top and this soil emptied into the litre of water. The mixture was thoroughly shaken to expel all air. Finally water was poured into the cylinder from a graduated vessel to bring the water level up to the 1800 c.c. mark. The volume of the water required for this is equal to the volume of the air contained in the potful of soil.

The soil was taken from a heap in one of the courts of the New Museums. It was poor garden soil, some shingle, but little organic matter. Rain had fallen recently (time of year, 1st week of March) so that the soil was quite damp. Two experiments were

* Joly and Smith, *Sci. Proc. Roy. Dub. Soc.* Aug. 1911.
† Sanderson, *Amer. Jour. Sci.* Sept. 1911.

made: (*a*) when the soil was rammed tight in the pot, (*b*) when the pot was loosely filled and just shaken down.

Another batch was dried on an iron plate over a burner and the experiments repeated with the dry soil. The following are the results, those for damp soil being the mean of three experiments.

TABLE III.

		Weight of Soil	Total Volume	Volume of Air	Percentage volume of the whole occupied by Air
Damp Soil	(*a*) tightly packed	1410 gms.	800 c.c.	100	12
	(*b*) loosely packed	930 ,,	800 ,,	350	44
Dry Soil	(*a*) tightly packed	1090 ,,	800 ,,	375	47
	(*b*) loosely packed	880 ,,	800 ,,	440	55

The estimates of the specific gravity of dry earth worked out from the two experiments quoted above are $\frac{1090}{325}$ and $\frac{880}{360}$ respectively, i.e. 2·45 and 2·56, with a mean of 2·5 very nearly. The specific gravity may now be used to effect the analysis of damp soil into dry earth and water. Taking the case of the tightly packed soil, if W is the weight of dry earth and w the weight of water in 1410 gms. damp soil we get

$$W \text{ gms.} + w \text{ gms.} = 1410 \text{ gms.},$$

$$\frac{W}{2{\cdot}5} \text{ c.c.} + w \text{ c.c.} = 700 \text{ c.c.},$$

whence $W = 1180$ gms. and $w = 230$ gms. For the loosely packed soil $W' = 800$ gms. and $w' = 130$ gms. These give 84 and 86 as the gravimetric percentages of dry earth in damp soil, a mean of 85 %.

The gravimetric and volumetric analysis of damp soil into the three elements—earth, water, and air—are stated in Table IV.

The soil around the bottom of the pipes will be damp and tightly packed, hence we may assume that 12 % of the total volume is air. If we assume that air is supplied to the pipe equally from all directions it follows that the radius of the sphere of collection when 3000 c.c. of air is drawn up the pipe is given by

$$\tfrac{4}{3}\pi\,(\text{radius})^3 \times \tfrac{12}{100} = 3000.$$

TABLE IV.

Tightly packed damp soil		
	Composition by volume	Composition by weight
Earth ...	59	85
Water ...	29	15*
Air	12	—
	100	100

This radius is just over 18 cms. so that the sphere of collection is well below the surface.

A litre of soil-air is in association with

$$\frac{1000}{100} \times 1410 \text{ gms. damp soil,}$$

or $$14100 \times \frac{85}{100} \text{ gms. dry soil,}$$

i.e. 12000 gms. dry soil.

Its emanation must therefore be obtained from the radium in this soil. The amount of radium required per gm. of soil in 12000 gms. dry soil to keep the emanation content of the air up to 200×10^{-12} curie is

$$\frac{200 \times 10^{-12}}{1{\cdot}2 \times 10^{4}} \text{ gm.,}$$

or $$1{\cdot}7 \times 10^{-14} \text{ gm.}$$

This is probably about one-seventieth† of the amount of radium actually present in a gm. of soil (mean value of radium content of sedimentary soils $= 1{\cdot}1 \times 10^{-12}$ gm. per gm. of soil‡). Sanderson§, working with the sandstone soil mentioned above (37 °/₀ air), obtains 9×10^{-14} as the equivalent radium content in gm. per c.c.

* A set of experiments in which damp soil was dried by being heated on an iron plate over a burner gave a loss of 18°/₀; a part of this loss, however, may be due to destruction of organic matter.

† In *Proc. Camb. Phil. Soc.* vol. XVI. I found that a damp soil in a bottle contributed emanation corresponding to about one-sixth of its radium content. In this case the soil was subjected to a reduced pressure when its emanation was removed to the testing vessel, and this might account for the greater amount of emanation removed in this case than in the gentler method of water aspiration.

‡ From the work of Strutt, Joly and others.

§ *Loc. cit.*

of earth, or approximately 3×10^{-14} gm. of radium per gm. of earth.

Very deep Pipes.

In November two pipes were inserted in the lawn outside the Laboratory to depths of 340 cms. and 420 cms., i.e. much greater than before, in order to test whether the emanation content of the soil-air was greater at greater depths. The 340 pipe gave an average leak of 86 for three readings, and the 420 pipe an average of 60 for four readings (variation from 84 to 22), so that no decisive results were obtained.

Relative Amounts of Radium and Thorium Emanation in the Soils.

When the testing vessel used by the author is rapidly filled with air containing radium emanation, and the electrical leak observed, the variation of the leak with the time is as shown in fig. 1. Initially the leak is simply due to the emanation breaking up. At once Rad. A, B, C, etc. begin to accumulate and also to disintegrate, and the conductivity of the air rises. At an interval from 10—20 minutes after filling the vessel there is a temporary maximum (due to Rad. B being rayless), after which the curve goes on rising for 3 hours when Rad. A, B, C attain equilibrium with the emanation present. The curve then bends over and finally drops exponentially, obeying the decay law of radium emanation.

The curves obtained by the author were got by drawing air out of the soil, letting it stand for a while to allow the thorium emanation to decay to an infinitesimal amount, and then rapidly filling the vessel with it. The average curve is drawn in three parts in fig. 1, *RA* is the curve for the first 12 minutes, *RB* the curve for the first hour, and *RC* the curve for the first 3 hours. The heights at the beginning, first maximum and second maximum, are approximately proportional to 3, 4 and 5·5. Knowing then the ordinate of the first maximum it is possible to get the initial ordinate by multiplying the former by $\frac{3}{4}$ (·73 more exactly).

If the testing vessel is suddenly filled with thorium emanation the leak obtained gives a much simpler curve. Thorium emanation decays exponentially to half value in about 53 seconds. The next product Th. A has a half period of only ·14 secs., while Th. B, which emits no α-rays, has a half period of 10·6 hours, and Th. C, which emits α-rays, a half period of 55 mins. In less than a second, therefore, Th. A is practically in equilibrium with

the Th. emanation, and the two decay together to half value in about 53 seconds. The growth of Th. B and Th. C is relatively small, so that the observed curve is practically a simple exponential curve with half value 53 seconds, followed by an almost negligible portion going to half value in a much longer time.

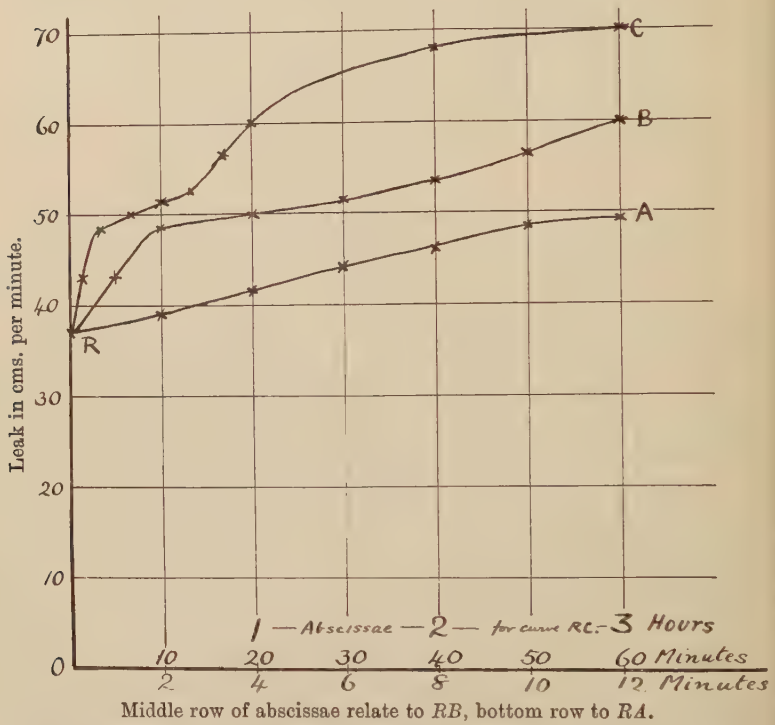


Fig. 1. Curve showing the variation with time of the electrical leak in a vessel containing air and a little radium emanation, the normal air leak being deducted.

If the testing vessel is suddenly filled with a mixture of radium and thorium emanations the curve obtained for the leak is the sum of the curves obtained for the two leaks. The shape of the curve depends on the relative proportions of the two emanations, but it will always contain an initial steep part due to the decay of thorium emanation, followed after the elapse of 10 minutes or so by the gradual rise due to the growth of the radium active deposit. Fig. 2 shows a possible curve. From the ordinate of the point A we can, by utilising the results from the curves in fig. 1, obtain the initial ordinate OR due to the radium emanation,

whence it follows that the remaining portion RT of the initial leak is the initial leak due to the thorium emanation. The initial curve of growth RH of the radium emanation can also be calculated from RA (Fig. 1), and it will be found that the ordinates of the curve TH, measured from RH, drop to half value in 53 seconds.

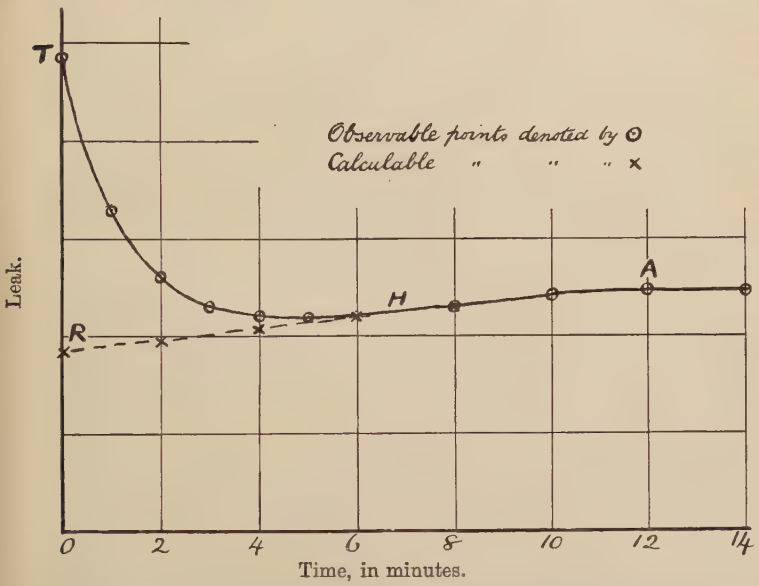


Fig. 2. Curve showing the variation with time of the leak in the testing vessel when the air contains radium and thorium emanations.

Calculation of the Relative Amounts of Radium and Thorium Emanations from the Ratio of OR to RT (fig. 2).

Let N_r, N_t be the initial amounts of radium and thorium emanations present, and λ_r, λ_t their radio-active constants. The rates at which the emanations break up are $\lambda_r N_r$ and $\lambda_t N_t$ respectively. The ionisation produced by the radium emanation break-up is due to the expulsion of one α-particle per atom of radium emanation breaking up, but the ionisation produced by the break-up of the thorium emanation is due (owing to the short life of Th. A) to the expulsion of two α-particles per atom of thorium emanation disintegrating. The ionising powers of all these α-particles have not been measured up to the present, so that we will assume as a first approximation that they are equal, whence we get

$$\frac{\lambda_r N_r}{2\lambda_t N_t} = \frac{OR}{RT},$$

and thus

$$\frac{N_r}{N_t} = 2\frac{\lambda_t}{\lambda_r}\cdot\frac{OR}{RT}$$
$$= 2\frac{1{\cdot}31\times10^{-2}}{2{\cdot}08\times10^{-6}}\cdot\frac{OR}{RT}.$$

The value of the ratio $\frac{OR}{RT}$ has been determined for the air drawn up the pipes mentioned in my previous papers. The pipes go down to the depths mentioned in Table V. *A* is a much wider pipe than the others; these are 7 metres long and $2\frac{1}{2}$ mm. internal bore. *A* is in soft garden soil; *B*, *C*, *D*, *G* are in the (rolled) lawn.

It is not possible to fill the vessel instantly. With the pipe *A* half a minute was required, with the others up to three-quarters of a minute. The point *T* therefore of fig. 2 is not well defined. The gas rushes in fastest when communication between vessel and pipe is first opened up, so I have taken *T* half-way in time between the times of opening up communication and the time when the vessel was practically full. The readings of the leak were begun as soon as possible—almost as soon as the vessel was filled.

A slight error in the relative amounts of the emanation will be caused if the air already in the pipe is passed into the vessel. For this air contains nearly its share of radium emanation, but far less than its share of thorium emanation. To remedy this a gentle stream of air was in some cases kept going through the pipe before connection to the testing vessel was made.

It was also found that when the vessel was very rapidly filled with gas (filled in 10 seconds, say) through short lengths of rubber or glass tubing, or through the calcium chloride drying tube, the gas became intensely ionised, and this ionisation gave a leak in the testing vessel which, in some cases, did not decay to zero for some minutes. Its decay was faster than that of thorium emanation and its presence would have been fatal to any accuracy in my experiments. To get rid of this effect a strong electric field was applied to the gas before entering the vessel. The field was set up between two concentric brass tubes 25 cms. long, and 2·4 and 2·5 cms. in diameter. The air passed down the annular space between the tubes. The outer tube was earthed and a potential of 320 volts applied to the inner tube. Even with this field on the ionisation just mentioned reached the testing vessel when the rush of gas was very large. With a long "compo" pipe, similar to the pipes used to get the air out of the soil hanging with its free end in the air, the effect was not noticeable even when the electric field was not applied. The addition of this pipe to the calcium chloride tube increased the time of filling from

$\frac{1}{4}$ minute to $\frac{3}{4}$ minute. The effect seems to depend largely on the velocity of the air stream filling the testing vessel, and the long lengths of compo pipe used seemed sufficient to reduce the velocity below that which caused this secondary ionisation.

Table V. gives the results, and figs. 3, 4, 5 the curves obtained in three of the cases. In those diagrams the height of the horizontal line OL represents the normal air leak taken just previous

TABLE V.

Pipe	Date 1911 and 1912	Initial Radium Emanation leak OR	First observed Thorium Emanation leak	Initial Thorium Emanation leak (corrected for decay during filling of vessel) RT	$\frac{OR}{RT}$
A (60 cms.)	Feb. 15	2, 5 } 4	25	32, 29 } 31	$\frac{4}{31} = \cdot 13$
	,,		22		
B (76 cms.)	Nov. 15	15	21	23	
	Dec. 10	9	20	27	
	Dec. 11	19 } 14	20	33 } 32	$\frac{14}{32} = \cdot 44$
	Dec. 20	12	24	33	
	Feb. 12	14	24	33	
C (152 cms.)	Feb. 26	18	17	21	
	,, 28	14 } 14	16	24 } 21	$\frac{14}{21} = \cdot 67$
	Mar. 5	9	13	19	
D (229 cms.)	Mar. 10	40	26	38	$\frac{40}{38} = 1 \cdot 0$
G (420 cms.)	Feb. 14	46, 50 } 48	16	20, 25 } 23	$\frac{48}{23} = 2 \cdot 1$
	Mar. 10		20		

to filling the vessel with the soil-air. The short horizontal lines give the average leaks over the interval of time indicated by their lengths. The curve THA is drawn as closely as possible through the middle point of these lines. The dotted vertical lines with numbers affixed show how nearly the time of decay of the curve HT agrees with that of thorium emanation. The shaded column represents in width the time required to fill the vessel. The line OT is drawn up the centre of this column. The position of T was obtained by the joint method of continuing

the thorium emanation curve backwards, and by making RT equal to twice the intercept of the vertical line between HT and HR taken a little less than a minute later.

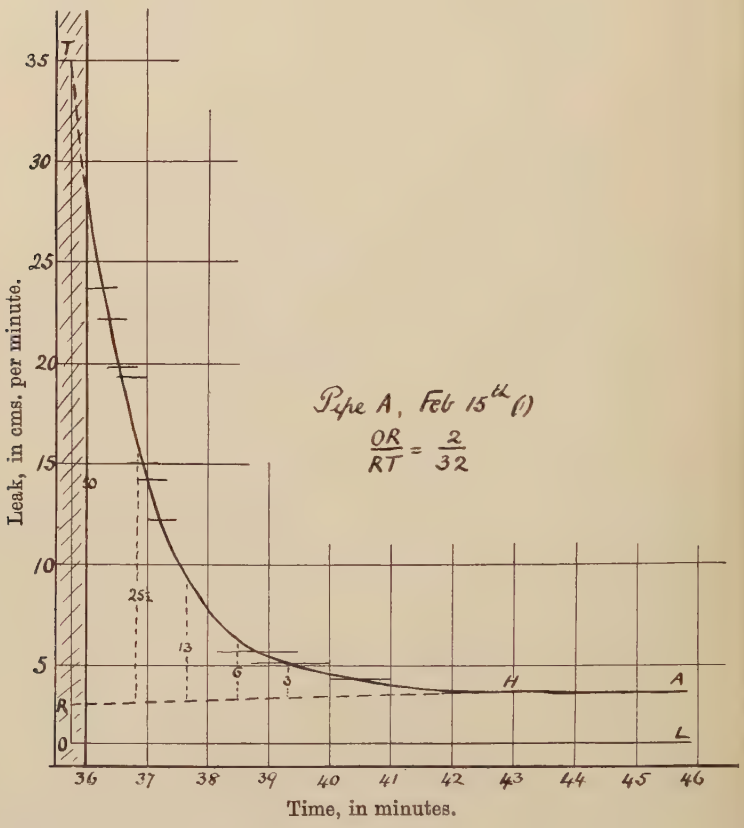


Fig. 3.

Applying the formula

$$\frac{N_r}{N_t} = 2 \times \frac{1{\cdot}31 \times 10^{-2}}{2{\cdot}08 \times 10^{-6}} \cdot \frac{OR}{RT}$$

to the mean values of the ratio $\frac{OR}{RT}$ given in the last column of Table V. we obtain the following numbers for the ratio of the amount of radium emanation to the amount of thorium emanation.

In the air near end of Pipe				*A*,	1600
"	"	"	"	*B*,	5500
"	"	"	"	*C*,	8600
"	"	"	"	*D*,	13000
"	"	"	"	*G*,	26000

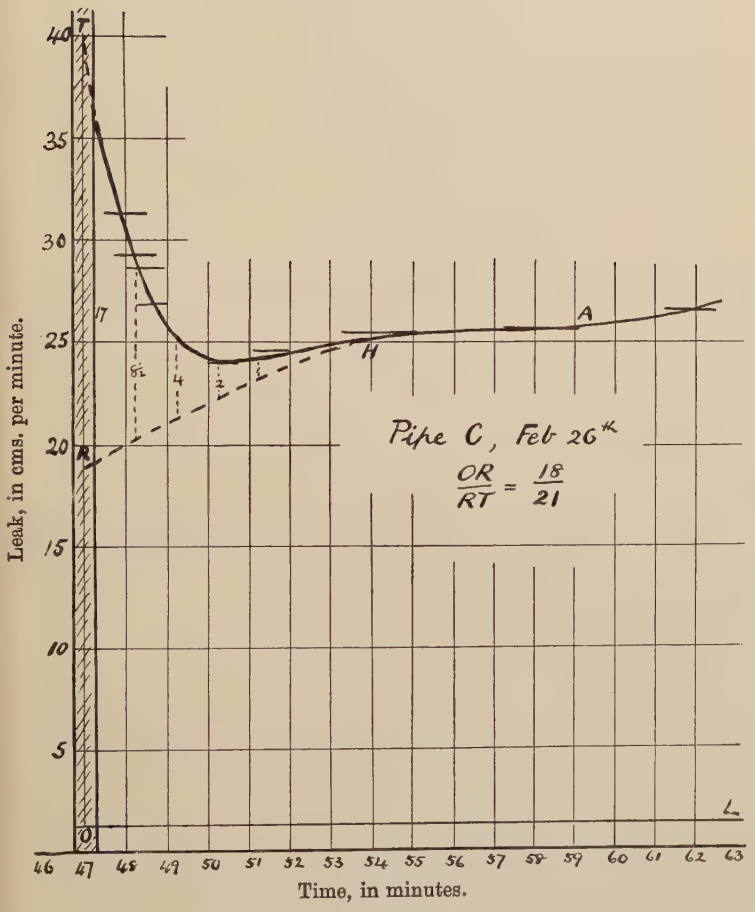


Fig. 4.

The ratio increases rapidly as the depth increases.

It is now possible to get an estimate of the relative amounts of radium and thorium in the soil, or at least the relative amounts of radium and thorium that contribute emanation to the air in the soil.

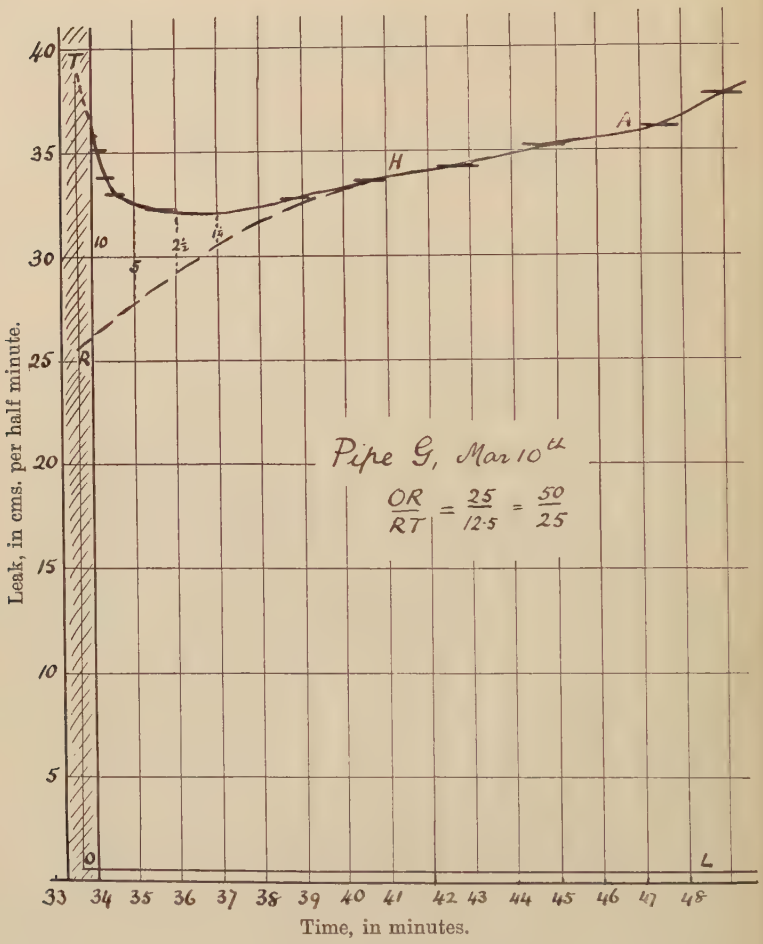


Fig. 5.

Let N_R and N_T be the amounts of radium and thorium in any given quantity of soil, and λ_R, λ_T the radio-active constants of radium and thorium. Then if N_r, N_t are the amounts of radium and thorium emanations in the same quantity of soil we get

$$\lambda_R N_R = \lambda_r N_r,$$
$$\lambda_T N_T = \lambda_t N_t;$$
$$\therefore \frac{N_R}{N_T} = \frac{\lambda_T}{\lambda_R} \cdot \frac{\lambda_r N_r}{\lambda_t N_t} = \frac{\lambda_T}{\lambda_R} \times 2 \times \frac{OR}{RT}$$
$$= \frac{7 \times 10^{-10}}{1{\cdot}1 \times 10^{-11}} \times 2 \times \frac{OR}{RT}.$$

Take the air in the soil around the pipe C (for which the mean value of the radium emanation content is given in Table I) then

$$\frac{OR}{RT} = \frac{14}{21} \text{ (Table V.)};$$

$$\therefore \frac{N_R}{N_T} = \frac{196 \times 10^{-19}}{23 \times 10^{-11}} = 8 \times 10^{-8}.$$

Sanderson* gets 7×10^{-8} for this ratio, working with a pipe going 130 cms. deep.

If further we assume that the mean radium content of the soil is $1{\cdot}1 \times 10^{-12}$ gms. per gm. it follows that the thorium content of the soil is

$$\frac{1{\cdot}1 \times 10^{-12}}{8 \times 10^{-8}} = 1{\cdot}4 \times 10^{-5} \text{ gm. per gm.}$$

This is about the right order, whence it seems that the two emanations have equal chances of escaping from their source in the solid particles to the air around these particles.

Examination of various Earths.

In the above experiments the air was drawn out of the soil and in the soil the emanations are in radioactive equilibrium with their sources. A series of experiments has also been carried out in which the soils were confined in bottles. At intervals extending over some days a bottle was taken and connected up through a calcium chloride tube to the testing vessel which had been previously exhausted. The clips were then opened and air rushed through the bottle carrying its gaseous contents into the testing vessel. The leaks were then taken as described above and the values of OR, RT, AL (see figs. 1—5) calculated from the curves obtained.

If the period of resting is greater than ten minutes the thorium emanation will have attained radioactive equilibrium but the radium emanation requires nearly a month to reach the steady state. Knowing however the time of resting it is possible from the amount of emanation accumulated to calculate the equilibrium amount.

Sometimes three "sweep-outs" were made on the same afternoon in order that all the emanation that had accumulated should be swept out. It was found that quite a measurable amount of radium emanation was obtained at the second and third times showing either that the first sweep-out was not exhaustive or else that, in the interval between two sweep-outs, radium emanation that had originally been occluded in the particles had, on account

* *Loc. cit.*

of the diminution of its partial pressure in the air, escaped from the solid into the air. The total amount of radium emanation collected on the same afternoon was taken as the accumulation since the last day on which the gas had been removed. Unfortunately any thorium emanation left behind at the first sweep-out cannot be recovered in a second sweep-out for it will have decayed to a negligible amount. The amounts of thorium emanation obtained in each sweep-out should be the same, for its equilibrium amount is quickly reached.

It was observed that the radium emanation removed by the sweep-out method was usually less than that obtained in the former experiments* in which a partial vacuum was applied to the contents of the bottle.

Four varieties of earths have been tried: gault (from the Newmarket Road pit), chalk (from the upper pit at Cherryhinton), soil (from just below the surface in the court of the museum adjoining the laboratory), and silver sand. They were all in a dry state, the gault had been lying openly in the laboratory for some months and the others were dried over a burner. The silver sand had been previously washed. The chalk and soil were sifted through a sieve of 9 mm. mesh; the gault was in slightly larger fragments.

The results obtained for gault are given in Table VI.

The mean equilibrium values for the sweep-out readings are

$$AL = 15, \quad OR = \cdot 73\dagger \times AL = 11, \quad RT = 25.$$

We have, therefore, for gault

(1) $$\frac{N_r}{N_t} = 2 \times \frac{1{\cdot}31 \times 10^{-2}}{2{\cdot}08 \times 10^{-6}} \times \frac{11}{25} = 5400.$$

(2) Apparent radium content

$$= \frac{15 \times 13 \times 10^{-12}}{1940} = \cdot 10 \times 10^{-12} \text{ gm. per gm.}$$

(3) By using the formula

$$\frac{N_R}{N_T} = \frac{7 \times 10^{-19}}{1{\cdot}1 \times 10^{-11}} \times 2 \times \frac{11}{25},$$

we get

$$\text{Apparent thorium content} = \cdot 2 \times 10^{-5} \text{ gm. per gm.}$$

By previous chemical treatment followed by ionisation analysis Strutt‡ found the radium content of Cambridge gault to be 1×10^{-12} gm. per gm. Similarly Joly§ found the thorium content

* *Proc. Camb. Phil. Soc.*, vol. xvi. pp. 348—354.

† See p. 519.

‡ *Proc. Roy. Soc.*, 78 A, 1906–7. Results corrected by Eve.

§ *Phil. Mag.*, Aug. 1910.

of clays of various natures to average 1×10^{-5} gm. per gm. The results that I have obtained show that only a small proportion of the total emanation generated in the gault reaches the air surrounding the particles.

TABLE VI. *Gault.*

A bottle of volume 1790 c.c. was filled with 1940 gms. of dry gault. Volume of air left in bottle 1200 c.c.

Date 1912	Period of Accumulation in days	Remarks	*AL*	*OR*	*RT*	Equilibrium value of *AL* calculated from the observed value and the growth curve of radium emanation
Jan. 3	—	Filled and well exhausted. Tested half an hour later.	·2	·2	23	
„ 19	16	Only swept out once	11·7	8·5	25	
„ 22	3	Swept out three times in same afternoon	(1) 5·1 (2) 1·9 (3) ·5	3·8 1·4 ·3	29 25 26	
		Total in 19 days	14·5	10·7		15·0
Feb. 21	30	Swept out three times in same afternoon	(1) 11·8 (2) 2·7 (3) ·6	8·9 2·0 ·5	23 30 29	
		Total	15·1	11·4		15·2
Mar. 21	29	Swept out three times in same afternoon	(1) 9·5 (2) 2·6 (3) 1·4	8·0 2·0 1·0	22 25 23	
		Total	13·5	11·0		13·7
„ 23		Volume of air left in bottle found*		Mean	25	15
„ 27	4	Radium emanation accumulation tested as in previous paper*. Second result got an hour later	(1) 6·0 (2) ·6 6·6			15·7

* *Proc. Camb. Phil. Soc.*, vol. xvi. pp. 348—354.

TABLE VII. *Chalk.*

A bottle of volume 4090 c.c. was filled with 4140 gms. of dry chalk. Volume of air left in bottle 2640 c.c.

Date 1912	Period of Accumulation in days	Remarks	*AL*	*OR*	*RT*	Equilibrium value of *AL* calculated from the observed value and the growth curve of radium emanation
Jan. 3	—	Filled and exhausted				
„ 31	28	Two sweep-outs made	(1) 3·0	2·1	4·0	
			(2) 1·4	1·0	2·5	
		Total	4·4	3·1		4·4
Feb. 27	27	Swept out; not tested				
Mar. 18	20	Only one sweep-out made	2·9	2·1	7·0	
„ 19	1	Three sweep-outs made on same day and also a slight exhaustion applied	(1) 1·5	1·1	7·5	
			(2) ·5	·4	4·0	
			(3) ·2	·2	2·0	
		Total for 21 days	4·7	3·4		4·8
„ 20	1	Three sweep-outs made	(1) ·6	·4	2·5	
			(2) ·2	·2	2·5	
			(3) ·0	·0	2·5	
		Total	·8	·6		4·8
„ 23	—	Volume of air left in bottle found		Mean	4	4·6
„ 27	4	Radium emanation accumulation tested as in previous paper; one exhaustion only	2·7	—	—	5·3

The mean equilibrium values for the sweep-out readings are $AL = 4{\cdot}6$, $OR = 3{\cdot}4$, $RT = 4$, whence we get for chalk

(1) $\frac{N_r}{N_t} = 11000.$

(2) Apparent radium content $= {\cdot}014 \times 10^{-12}$ gm. per gm.

(3) Apparent thorium content $= {\cdot}01 \times 10^{-5}$ gm. per gm.

Strutt* found $\cdot 12 \times 10^{-12}$ for the radium content of Cherry-hinton chalk and Joly* found $< \cdot 05 \times 10^{-5}$ for the thorium content of chalk from the Isle of Wight. Here again it is probable that only a small proportion of the emanation generated escapes from the solid.

TABLE VIII. *Earth from Court adjoining the Cavendish Laboratory.*

A bottle of volume 1710 c.c. was filled with 2130 gms. of dry earth. Volume of air left in bottle 950 c.c.

Date 1912	Period of Accumulation in days	Remarks	*AL*	*OR*	*RT*	Equilibrium value of *AL* calculated from the observed value and the growth curve of radium emanation
Jan. 3	—	Filled and exhausted				
Feb. 1	29	Three sweep-outs made on the same day	(1) 7·9	5·8	7	
			(2) 3·2	2·4	19	
			(3) 1·2	·9	10	
		Total	12·3	9·1		12·4
Feb. 20	19	„	(1) 8·8	6·3	6·5	
			(2) 3·3	not taken		
			(3) ·8	·6	6·5	
		Total	12·9			13·5
Mar. 22	31	„	(1) 8·4	6·1	5	
			(2) 3·0	2·2	8	
			(3) 1·5	1·1	6·5	
		Total	12·9	9·4		13·0
„ 23	—	Volume of air left in bottle found.		Mean	8	13
„ 27	4	Radium emanation accumulation tested as in previous paper. Two exhaustions made.	(1) 7·3			
			(2) 1·0			
			8·3			16·0

* *Loc. cit.*

The mean equilibrium values for the sweep-out readings are $AL = 13$, $OR = 9{\cdot}5$, $RT = 9$, whence we obtain for this earth

(1) $\frac{N_r}{N_t} = 15000.$

(2) Apparent radium content $= {\cdot}08 \times 10^{-12}$ gm. per gm.

(3) Apparent thorium content $= {\cdot}05 \times 10^{-5}$ gm. per gm.

For surface soil Sanderson* obtained $\cdot 1 \times 10^{-5}$ for the thorium content.

Table IX. *Silver Sand.*

Quantity taken = 3500 gms.
The equilibrium values obtained were

$$AL = 1{\cdot}2, \quad OR = {\cdot}9, \quad RT = 1{\cdot}8,$$

whence

(1) $\frac{N_r}{N_t} = 6000.$

(2) Apparent radium content $= {\cdot}004 \times 10^{-12}$ gm. per gm.

(3) Apparent thorium content $= {\cdot}007 \times 10^{-5}$ gm. per gm.

For sand Sanderson* got $< 0{\cdot}00 \times 10^{-6}$ gm. per gm. for the thorium content.

The above results were obtained by what may be called the statical method. Sanderson* used what may be called a dynamical method. The author hopes to apply soon this second method to the same specimens of earths so as to check the results already obtained.

Summary.

1. The amounts of radium emanation in the air of different soils have been measured at intervals extending over a year. For depths of 100—150 cms. in gravelly soil the amount is, on the average, about 200×10^{-12} curie per litre, or 2000 times as much as there is usually in the atmospheric air.

2. Experiments showed that a litre of soil-air was in association with 14000 gms. of damp soil (12000 gms. when dry), whence the apparent radium content of the soil is $1{\cdot}7 \times 10^{-14}$ gm. per gm. of (dry) soil. As the actual radium content is more likely to be seventy times it follows that little of the emanation generated

* *Loc. cit.*

in the solid particles of the soil can escape under normal conditions into the air around them. This is a remarkable result and experiments on this point are being continued.

3. The proportion of radium emanation to thorium emanation in soil-air has been measured for various depths, and the ratio has been found to increase from 1600 near the surface to 26000 at a depth of 400 cms. At a depth of 150 cms. it is 8600, whence taking the radium content of the soil as $1{\cdot}1 \times 10^{-12}$ gm. per gm. the thorium content works out as $1{\cdot}4 \times 10^{-5}$ gm. per gm. This is of the right order.

4. The amounts of radium and thorium emanations have also been measured for varieties of earths confined in bottles, also the equivalent radium and thorium contents of these earths. The results are at follows:—

TABLE X.

	Ratio of amount of radium emanation to amount of thorium emanation	Apparent radium content	Apparent thorium content
		gm. per gm.	gm. per gm.
Gault	5400	$\cdot10 \times 10^{-12}$	$\cdot2 \times 10^{-5}$
Chalk	11000	$\cdot014 \times 10^{-12}$	$\cdot01 \times 10^{-5}$
Earth	15000	$\cdot08 \times 10^{-12}$	$\cdot05 \times 10^{-5}$
Sand	6000	$\cdot004 \times 10^{-12}$	$\cdot007 \times 10^{-5}$

I wish to accord my best thanks to Prof. Sir J J. Thomson for his helpful advice.

On a theory of the dissymmetrically distributed secondary Röntgen Radiation.

By J. A. Crowther, M.A., St John's College.

[*Read* 11 March 1912.]

When Röntgen radiation falls upon a radiator it causes it to emit cathode rays in considerable quantity. Some of these escape from the surface of the radiator, but in most cases the bulk of the rays are stopped within the radiator itself. On almost any theory of Röntgen radiation the stoppage of these particles must give rise to a further production of Röntgen rays. So far as I am aware, however, this type of secondary Röntgen radiation does not seem to have been experimentally observed.

In the course of some experiments on the distribution of secondary Röntgen radiation, it was found that the scattered radiation was not distributed symmetrically round the radiator as was to be expected on the ordinary theories of the phenomenon, but that there was always an excess of radiation in the forward or emergence direction as compared with that in the reverse direction. The fact that the return radiation followed very closely the distribution assigned to it on the usual theories of the scattering of Röntgen rays suggested that this excess forward radiation might be due to some other source other than the pure scattering of the primary beam. In the present paper I wish to consider the possibility of this excess radiation being due to the stoppage of the cathode particles in the radiator, to which we have already alluded.

Before enquiring into the consequences of this hypothesis it may be desirable to summarise briefly the properties of this excess radiation as they have been so far determined. They may be expressed as follows.

(1) For a given radiator and for primary rays of given hardness the excess radiation in any direction is directly proportional to the thickness of the radiator.

(2) The total excess radiation round the radiator decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator.

(3) Within the limits of experimental error the hardness of the excess radiation is the same as that of the primary from which it is produced.

(4) If $E_\theta . \delta\theta$ is the intensity of the excess radiation between the angles θ and $\theta + \delta\theta$ with the primary beam

$$E_\theta . \delta\theta = \frac{2}{b} E . e^{-\theta/b} \theta . \delta\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots (a),$$

where E is the whole intensity of the excess radiation round the radiator, and b is a constant depending only on the quality of the primary beam and the substance of the radiator.

(5) The value of b decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator. It is independent of the thickness of the radiator.

Let us consider each of these results separately on the hypothesis that this excess radiation is due to the stoppage within the radiator of the cathode rays excited in it by the incident primary beam.

(1) Since the excess radiation arises from the transformation of the cathodic radiation, its whole intensity must be proportional to the total number of cathode rays stopped in the radiator. A certain quantity of these rays emerge from the radiator and thus do not add their quota to the secondary beam. The thickness of matter which can be traversed by a cathode ray is however so small that only the rays formed in the layer very near the surface of the radiator can thus escape, and these form, for any radiator used in the experiments, a very small fraction of the total cathode radiation. The number stopped may thus be taken as simply proportional to the number produced, that is to say, for primary rays of a given quality and a radiator of a given material, simply proportional to the intensity of the incident primary beam and the thickness of the radiator.

(2) Considering rays of differing hardness and radiators of different materials, experiments have shown that the production of cathode radiation decreases as the primary rays become harder, and increases as the atomic weight of the radiator is increased. We thus obtain the results enunciated in (2). The data available at present do not enable us to apply any numerical test to the hypothesis, but the general results are quite in accordance with what would be anticipated from the theory.

(3) The hardness of a Röntgen pulse depends only on the velocity of the cathode ray from which it is produced. Whiddington has recently shewn that the velocity of the secondary cathode rays produced by the action of a given Röntgen beam is exactly that of the primary cathode rays producing the primary Röntgen beam. It follows that the Röntgen rays produced by the stoppage of these secondary cathode rays should be of the same hardness as that of the primary Röntgen beam itself, as is found to be the case.

(4) We come now to the distribution of the excess radiation. This is a more difficult problem and will involve further assumptions. The author has shewn in a previous paper that the distribution of a parallel pencil of β-rays, after transmission through a thin sheet of matter, may be represented in the form

$$E_\theta . \delta\theta = \frac{2}{n\alpha^2} . e^{-\theta^2/n\alpha^2}\, \theta . \delta\theta \ldots\ldots\ldots\ldots\ldots\ldots (b),$$

where n is the number of collisions made by the β-particle in its passage through the radiator, and α the mean deflection per collision. This expression reduces to (a) if we omit the constant E, and write b for the quantity $n\alpha^2$. On the other hand the excess radiation cannot be due to the scattering of the primary Röntgen beam because the value of E is found experimentally to be only a very small fraction of that of the whole intensity of the incident primary beam, instead of being equal to it as should be the case if the expression referred to the primary beam as a whole. Further the value of b is independent of the thickness of the radiator, whereas if the expression referred to the primary beam it should be proportional to it.

We have noted the resemblance of the distribution curve for the excess radiation to that for β-rays. Let us assume:

(1) That the cathode particles given out by the substance of the radiator under the action of the primary rays are projected in the line of the primary beam.

(2) That in passing through the radiator they become scattered, their scattering following the same laws as have been observed for the similar but faster moving β-rays.

(3) That after traversing a certain mean thickness of the radiator, depending on the nature of the radiator and the velocity of the rays, a certain fraction of them are transformed back into Röntgen radiation.

(4) That a Röntgen pulse so produced follows the direction of the cathode particle producing it at the moment when the transformation took place.

We will discuss the evidence for and against these assumptions later. Let us consider for the moment the mode of production of the excess radiation on these assumptions.

The primary rays striking the first layer of the radiator produce in addition to the true scattered radiation a quantity of cathode particles, which are projected in the direction of the primary beam itself; that is to say they form a pencil of rays parallel to the primary beam. After passing through a thickness of matter t they will be distributed about this direction in the way represented by (b).

Supposing at this point a certain fraction of the rays are in

some way transformed into Röntgen rays, and that the Röntgen ray produced continues the direction of the cathode particle producing it. As Röntgen rays undergo no deflexion in matter this Röntgen radiation will be distributed round the radiator in the same way as the cathode particles producing it. That is to say the intensity in any direction θ will be proportional to the expression on the right-hand side of equation (b) where the constants n and α refer not to the primary rays but to the cathode rays produced by them in the substance of the radiator. We have seen experimentally that the distribution of the excess radiation can be represented by such an expression, and that the constants of the expression do not refer directly to the primary Röntgen rays.

As n represents the number of collisions made by the *cathode* particle before its transformation, it is evident that the value of $n\alpha^2$ will be independent of the thickness of the radiator, provided that it is sufficiently great compared with the thickness t. Direct experiments on the scattering of cathode rays, in a suitable form for calculation, are unfortunately still wanting. We can, however, with some degree of certainty, make extrapolation from the results on the scattering of the β-rays. It has been shewn* that the scattering varies inversely as the fourth power of the velocity of the rays. Assuming this law we can shew that the thickness t for the rays used in these experiments is probably less than $\frac{1}{100}$th of a millimetre. It is therefore negligibly small compared with the thickness of the radiators.

The value of the constant E in equation (a) is equal to the product of the transformation coefficients of the primary Röntgen rays into the secondary cathode rays, and of the latter into secondary Röntgen rays. Quantitative experimental data on the production of cathode rays by primary Röntgen radiation are very scanty. It is known that, in general, the emission diminishes as the primary rays become harder, and further that the emission by aluminium, and metals in general, is much greater than from substances of low atomic weight such as filter paper. We should expect that the intensity of the excess radiation should be greater from soft than from hard primary rays, and much greater for aluminium than for filter paper. Such has been found to be the case.

Without further assumptions, we cannot make any definite predictions as to the variation of the constant b with the hardness of the rays or the nature of the radiator. The whole question of the transformation of a cathode into a Röntgen ray is at present involved in the deepest obscurity. If however we make the assumption that the transformation takes place after a definite number of collisions, then b should vary with the velocity of the

* J. A. Crowther, *Roy. Soc. Proc.* A, vol. LXXXIV. p. 226, 1910.

cathode rays producing the radiation. It has been shewn experimentally that for β-rays the value of α^2 varies inversely as the fourth power of the velocity. If this holds also for cathode rays b should vary inversely as the fourth power of the velocity of the secondary cathode rays. As the velocity of these is the same as that of the cathode rays which produced the primary Röntgen rays we should be able to calculate it from the equivalent spark gap of the focus tube.

The velocity of the cathode rays in the tube is proportional to the square root of the equivalent spark gap. The value of b which is inversely proportional to the fourth power of the velocity should be inversely proportional to the square of the spark gap. For various reasons the method is not very reliable, especially when the bulb is very soft. Results recently obtained by the author, however, shew an approximate constancy for the product of b into the square of the equivalent spark gap, both for rays of different hardnesses and for different radiators. It is hoped to make more direct experiments on this point, and to measure the actual velocity of the cathode rays produced, and the corresponding values of b.

The scattering of a beam of cathode rays by aluminium is much greater than the scattering by an equal thickness of filter paper. We should expect therefore that the value of b would be much greater for aluminium than for filter paper under the same conditions. This is found to be the case.

The experimental distribution of the scattered Röntgen radiation may thus be explained at least qualitatively on our hypothesis with the help of the assumptions on p. 536. Of these, the first has been argued at length by Prof. Bragg*, and the second will probably be generally admitted; the difference between cathode and β-rays being one of velocity only. So little has yet been done on the obscure problem of the transformation by which the energy of a cathode particle becomes the energy of a Röntgen pulse that we are hardly in a position to discuss either assumption (3) or (4). With regard to (3) we may say that all the evidence so far collected shews that the whole of the energy with which the cathode particle strikes the anticathode is converted into Röntgen radiation when the transformation occurs at all, and that consequently the transformation must take place before the particle has lost any appreciable amount of its velocity, *i.e.* in a very small thickness of the anticathode, or the radiator.

That the Röntgen ray produced by the transformation of a cathode ray should follow the line of action of the ray producing it, as assumed in (4), would follow directly from the theory of the

* Prof. W. H. Bragg, *Phil. Mag.* xx. p. 385, 1910.

phenomena propounded by Prof. Bragg. It could be also explained on the ether pulse theory. There is also some experimental evidence in favour of this assumption. Some time ago Kaye* published some preliminary observations on the emission of Röntgen rays from thin metallic sheets. He allowed a stream of cathode rays to fall on a very thin metallic sheet, and measured the amounts of Röntgen radiation proceeding from the radiator on the two sides. He found that there was always an excess of Röntgen radiation on the side remote from that first struck by the cathode stream; that is to say in the direction of the incident cathode particles. In the case of aluminium the ratio rose as high as 3 : 1. As we have already seen that the cathode rays undergo some scattering before transformation, these results seem strongly to support the assumption that the Röntgen rays continue the direction of the cathode rays from which they take their rise.

In conclusion, then, it is seen that the experimental evidence so far available is not unfavourable to the assumptions we have found it necessary to make to explain our results. It is certainly desirable however that further experiments should be made on many of the points raised, and some are already in progress. It is hoped that they will throw further light on the problems involved.

* G. W. C. Kaye, *Proc. Camb. Phil. Soc.* Vol. xv. p. 269, 1909.

On the Different Internal Energies of a Substance. I. By R. D. Kleeman, B.A., Emmanuel College, D.Sc. (Adelaide), Clerk Maxwell Student of the University of Cambridge.

[*Read* 11 March 1912.]

Division of Internal Energy into Parts.

The internal energy of a substance may be divided into three parts, viz., (1) the kinetic energy of the molecules due to their motion of translation, (2) their internal molecular energy, and (3) the potential energy due to their attraction upon one another. These three parts will be considered in turn.

It is usually stated as an assumption that the kinetic energy of a molecule in a substance is the same as that in a gas at the same temperature. It is possible to obtain definite information on this point, from which it will appear that this loose statement must be considerably modified.

Suppose that a thermometer is placed in a perfect gas. It will assume the temperature of the gas through being bombarded by the gas molecules. From experience we know that if the gas be allowed to expand without doing external work the temperature indicated by the thermometer would remain the same, showing that the temperature it indicates is independent of the number of molecules impinging per second per cm.^{2} on its surface. Let us consider the effect of the attraction of the material of the bulb on the molecules of the gas. When a molecule gets into the zone of attraction of the bulb its velocity is increased, and each molecule thus impinges on the bulb with a greater velocity than it possesses when not under the influence of an external force. Now suppose the bulb covered with a material which exerts a much more powerful attraction on the surrounding gas molecules than the material of the bulb. Each molecule now impinges on the bulb with a much greater velocity than before. But we know from experience that the temperature indicated by a thermometer is independent of the outside material of its bulb. It appears therefore that the temperature indicated by a thermometer placed in a gas is regulated by the velocity of the molecules when not under the influence of an external force.

Suppose the thermometer is placed in a liquid. The temperature of the liquid and thermometer are equalized as before by the molecules of the liquid bombarding the bulb of the thermometer. Now there must exist a large number of points in a liquid, which like the molecules are in motion, at which the forces of the

surrounding molecules neutralize one another. It follows from the above result that the thermometer indicates a temperature corresponding to the velocity a molecule has when passing through one of these points. This velocity is the same as that it has in the gaseous state at the same temperature.

The same considerations apply to a solid. The motion of a molecule in a solid is, however, not migratory as in the case of a liquid or gas. It is probably more or less one of vibration like that of a pendulum. According to the foregoing the velocity of a molecule when it vibrates through a point at which the forces of attraction of the surrounding molecules is zero is equal to that it has in the gaseous state at the same temperature.

The effect of molecular attraction is to make the molecules in a mass of matter approach one another on 'collision' with a greater velocity than they would have if they did not possess this property. It follows therefore that the minimum velocity of a molecule corresponds to its velocity in the gaseous state at the same temperature, while the average velocity is larger, and as will be shown in a subsequent paper, much larger than this velocity.

In a previous paper* we have shown that in order to be able to calculate the energy necessary to separate the molecules of a substance by an infinite distance from one another we may suppose the molecules devoid of motion and distributed in space in a certain way. One of the conditions which determines this distribution is that the force on each molecule by the surrounding molecules must be zero. It follows therefore that the average energy necessary to remove a molecule from a substance to infinity is that expended when it is removed at the moment it has its minimum velocity. Since this minimum velocity is the same as the velocity in the gaseous state, the removal of the molecule does not change its kinetic energy due to its motion of translation. One part of the internal energy of a molecule in a substance consists therefore of kinetic energy of translation which depends only on the temperature of the substance.

This kinetic energy of a molecule can be easily calculated. Its kinetic energy in the gaseous state is $\frac{V^2 m_a}{2}$, where $V^2 = \frac{3RTm_H}{m_a}$ according to the kinetic theory of gases, V denoting its velocity at the temperature T, m_a and m_H the absolute mass of the molecule and that of a hydrogen atom respectively, and R the gas constant whose value is $8{\cdot}26 \times 10^7$. The kinetic energy at the temperature T is therefore equal to $\frac{3Rm_H}{2}T$.

* *Phil. Mag.*, April 1911, p. 537.

The internal energy of a molecule, which will be considered next, will be denoted by u_1. It may consist of kinetic energies of rotation and of potential energies due to the attraction of the atoms upon one another. In the case of a gas at a very low pressure the molecular internal energy will be denoted by u_a, since it then possesses special properties. We have then that if S_g denote the specific heat at constant volume in ergs of a gram of gas at a very low pressure, $S_g = \frac{1}{m_a}\left(\frac{du_a}{dT}\right)_v + \frac{3Rm_H}{2m_a}$ *. Measurements of the quantity S_g indicate that $\left(\frac{du_a}{dT}\right)_v$ is independent of the volume v of the gas if it is large, or the value of u_a of a molecule is independent, or at least very approximately so, of the number of collisions it undergoes per second with other molecules. From this it follows that $\left(\frac{du_a}{dv_m}\right)_T = 0$, where v_m denotes the apparent volume occupied by a molecule. The value of $\left(\frac{du_a}{dT}\right)_{v_m}$, determined from measurements of S_g, has always positive values. It appears therefore that the value of u_a is not influenced by the number of collisions per second the molecule undergoes, but by their violence.

When the molecules of a substance are under the influence of each others' attraction the value of u_1 of a molecule is very probably affected by the apparent volume v_m it occupies. According to what has gone before, the change in the value of u_a with increase of temperature is due to an increase in the violence of molecular collision and consequent change in its nature, for it is very unlikely that it is connected with the increase of the velocity through space. Now when the molecules of a substance are under each others' influence the nature of the collision of a molecule with another differs obviously in nature from that it would have if the substance existed in the state of a perfect gas at the same temperature. We have therefore good reason to believe that the values of $\left(\frac{du_1}{dT}\right)_{v_m}$ and $\left(\frac{du_1}{dv_m}\right)_T$ depend on v_m in such a case. We will see later that at present we are not able to test this directly.

The third part of the internal energy of a molecule in a substance is that due to the attraction of the molecules upon one another. We will denote it by U_1. Its value can be calculated if the law of molecular attraction is exactly known. The properties of U_1 depend therefore on those of this law, whose properties will therefore be further investigated in this paper.

* A differential coefficient in brackets indicates a partial differential coefficient obtained keeping the quantity constant indicated by the suffix.

It will now be seen that the internal heat of evaporation L_1 of a gram of matter into a vacuum, or the energy necessary to separate the molecules by an infinite distance from one another, is strictly given by

$$L_1 = \frac{1}{m_a}(U_1 + u_1 - u_a) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1).$$

The ordinary heat of evaporation of a liquid is therefore given by

$$L = L_1 - L_2 = \frac{1}{m_a}(U_1 + u_1 - U_2 - u_2),$$

where the suffixes 1 and 2 refer to the liquid and its saturated vapour respectively. In previous papers we have neglected $(u_1 - u_2)$ in comparison with $(U_1 - U_2)$, and the results obtained have justified this assumption.

The surface tension of a liquid is the amount of work done on increasing its area of surface by one cm². at constant temperature. Therefore if any change in the internal energy of the molecules takes place during the process it has to be applied in the form of heat, and therefore does not affect the value of the surface tension.

It will be of interest next to study more closely some of the quantities which depend on U_1, u_1, and $\frac{3Rm_H}{2}T$.

The Intrinsic Pressure.

The quantity U_1 of a substance can be connected very simply with its intrinsic pressure. The change in the part of the potential energy due to molecular attraction of unit mass of matter when its volume changes by dv at constant temperature is equal to $P_n . dv$, where P_n denotes the intrinsic pressure. Since this quantity is also equal to $dU_1 . \frac{1}{m_a}$, we have $P_n . dv = \frac{dU_1}{m_a}$ or

$$P_n = \frac{1}{m_a} . \left(\frac{dU_1}{dv}\right)_T = \left(\frac{dU_1}{dv_m}\right)_T = -\left(\frac{dU_1}{d\rho}\right)_T . \frac{\rho^2}{m_a},$$

where v_m denotes the molecular volume of a molecule and ρ the density of the matter.

A relation can now be obtained between the quantities P_n, U_1, and u_1. From thermodynamics we have $\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v$, where dQ is the amount of heat absorbed by unit mass of matter when it changes in volume by dv at the constant temperature T, and

$\left(\frac{dp}{dT}\right)_v$ is the increase of external pressure with increase of temperature dT keeping the volume constant. Now

$$dQ = dL_1 + p \,.\, dv = \frac{1}{m_a}(dU_1 + du_1 - du_a) + p \,.\, dv,$$

where $p \,.\, dv$ is the amount of heat absorbed due to the external work done. The above equation then becomes

$$P_n + \frac{1}{m_a}\left(\frac{du_1}{dv_m}\right)_T + p = T\left(\frac{dp}{dT}\right)_v \quad \ldots\ldots\ldots\ldots\ldots(2),$$

where $\left(\frac{du_a}{dv_m}\right)_T = 0$. If the intrinsic pressure of a substance could be exactly calculated or measured, this equation could be used to obtain some information about the quantity u_1. When the substance behaves as a perfect gas the above equation becomes $\left(\frac{du_1}{dv_m}\right)_T = 0$, which fits in with what we would expect from previous considerations.

Another relation of interest can be obtained. From thermodynamics we have

$$\left(\frac{dQ}{dp}\right)_T = T\left(\frac{dv}{dT}\right)_p, \quad \text{or} \quad \frac{1}{v}\left(\frac{dQ}{dv}\,.\,\frac{dv}{dp}\right)_T = \frac{T}{v}\left(\frac{dv}{dT}\right)_p.$$

Hence
$$P_n + \frac{1}{m_a}\left(\frac{du_1}{dv_m}\right)_T + p = -\frac{T\alpha}{\beta} \quad \ldots\ldots\ldots\ldots\ldots(3),$$

where α denotes the coefficient of expansion with increase of temperature at constant pressure, and β the coefficient of compression at constant temperature.

Equation (3) may be used to calculate the intrinsic pressure of a liquid. The value of p is then (as the results obtained will show) small in comparison with P_n. Since $(u_1 - u_a)$ may be neglected in comparison with $(U_1 - U_2)$, it is very probable that $\left(\frac{du_1}{dv_m}\right)_T$ may be neglected in comparison with $\left(\frac{dU_1}{dv_m}\right)$ or P_n. Assuming this to be the case for the present we obtain the simple equation

$$P_n = -\frac{T\alpha}{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4).$$

This equation probably gives the most reliable values of P_n for a liquid. Table I contains the values of P_n in atmospheres at different temperatures for a number of liquids calculated by means of the above equation. The data used are taken from Landolt and Börnstein's Tables. It will be seen that the intrinsic

pressure of a liquid is usually very much larger than the pressure of its saturated vapour.

TABLE I.

t^0	$\beta 10^6$	a	L cal. per grm.	ρ	$P_n = \frac{-Ta}{\beta}$ (atmos.)	$L\rho \times 42$ (atmos.)
Ether						
13·5	169	·001574	82·58	·7214	−2669	−2502
25·4	190	·001632	81·64	·7077	−2565	−2424
63	300	·001809	70·06	·6620	−2026	−1944
78·5	367	·001892	66·22	·6105	−1812	−1788
99	539	·001992	60·33	·6421	−1375	−1543
Benzene						
15·4	87	·001215	97·4	·8840	−4083	−3616
50·1	111	·001305	91·0	·8466	−3796	−3235
78·8	126	·001379	85·62	·8145	−3850	−2929
Chloroform						
0	101	·001107	62·45	1·5264	−2991	−3992
20	128	·001294	60·14	1·4885	−2970	−3763
40	162	·001484	57·87	1·4503	−2869	−3524
60	204	·001670	55·60	1·4108	−2726	−3295
Pentane						
0	229	·001465	85·85	·6454	−1747	−2328
20	318	·001589	79·99	·6262	−1337	−2103
40	416	·001721	75·55	·6062	−1294	−1923
60	486	·001830	71·66	·5850	−1260	−1761

In a previous paper* it was shown that $P_n = kp_c$, where p_c is the critical pressure and k a quantity which has the same value for all substances at corresponding states. It follows from this

* *Phil. Mag.*, Oct. 1910, p. 668.

equation that the ratio of the critical pressures of two substances is equal to the ratio of their intrinsic pressures at corresponding temperatures. The above values of P_n approximately satisfy these conditions. Thus the intrinsic pressures of the liquids ether and benzene corresponding to the temperatures $\frac{2T_c}{3}$ are 2756 and 3893 atmos. and their ratio is ·708. The corresponding ratio of the critical pressures is equal to ·733, and thus approximately equal to the former ratio. This is evidence that the assumption made as to the relative importance of U_1 and u_1 is correct.

In a previous paper* the writer deduced the formula $P_n = L_1\rho$ for the intrinsic pressure on the supposition that matter is evenly distributed in space, that is, does not consist of molecules, where L_1 denotes the energy necessary to separate the elements of mass of a gram of substance by an infinite distance from one another, and ρ the density of the substance. It was further assumed that the elements of mass did not undergo any change in their internal energy during separation. At low temperatures L_1 is equal to L, the ordinary heat of evaporation. Table I contains values of P_n obtained by the above formula, using the values of L calculated by Mills†. Comparing them with those obtained by equation (4) we see that matter behaves as if the above assumptions are approximately satisfied‡.

The Internal Heat of Evaporation.

According to an equation given in a previous part of the paper $L_1 = \frac{1}{m_a}(U_1 + u_1 - u_a)$. Hence

$$m_a{}^2\frac{dL_1}{dv_m} = \left(\frac{dU_1}{dv_m}\right)_T + \left(\frac{dU_1}{dT}\right)_{v_m}\frac{dT}{dv_m} + \left(\frac{du_1}{dv_m}\right)_T + \left(\frac{du_1}{dT}\right)_{v_m}\frac{dT}{dv_m} - \left(\frac{du_a}{dv_m}\right)_T - \left(\frac{du_a}{dT}\right)_{v_m}\frac{dT}{dv_m},$$

where $\left(\frac{du_a}{dv_m}\right)_T = 0$. By means of equation (3) the foregoing equation may be written

$$m_a\frac{dL_1}{dv_m} + p + \frac{T\alpha}{\beta} = \frac{1}{m_a}\left\{\left(\frac{dU_1}{dT}\right)_{v_m} + \left(\frac{du_1}{dT}\right)_{v_m} - \left(\frac{du_a}{dT}\right)_{v_m}\right\}\frac{dT}{dv_m} \quad \ldots(5).$$

If this equation is applied to a liquid in contact with its saturated vapour at a low temperature, $\frac{dL_1}{dv_m}$ can be evaluated since

* *Phil. Mag.*, Oct. 1910, p. 670.
† *Journal of Phy. Chem.*, Vol. VIII. p. 405 (1904).
‡ See also *Phil. Mag.*, Oct. 1911, p. 584.

L_1 is then very approximately equal to L the ordinary heat of evaporation. The other quantities on the left-hand side of the equation can be easily measured in all cases.

Let us suppose that $\left(\frac{du_1}{dT}\right)_{v_m} = \left(\frac{du_a}{dT}\right)_{v_m}$, which is very probably at least approximately true. The above equation may then be used to obtain the values of $\left(\frac{dU_1}{dT}\right)_{v_m}$ for different substances. Table II contains the values of $\frac{1}{m_a}\left(\frac{dU_1}{dT}\right)_{v_m}\frac{dT}{dv_m}$ at different

TABLE II.

Ether			Pentane		
t	$m_a\frac{dL_1}{dv_m}$	$m_a\frac{dL_1}{dv_m}+\frac{Ta}{\beta}$	t	$m_a\frac{dL_1}{dv_m}$	$m_a\frac{dL_1}{dv_m}+\frac{Ta}{\beta}$
13·5	− 5720	− 3051	0	− 5130	− 3383
25·4	− 5190	− 2625	20	− 4610	− 2273
63	− 3840	− 1834	40	− 3600	− 2306
78·5	− 3480	− 1668	60	− 2810	− 1550
99	− 3200	− 1825			

temperatures for a number of substances calculated in this way, using the values of $\frac{Ta}{\beta}$ obtained previously. It will be seen that they are all negative. Since $\frac{dT}{dv_m}$ is positive $\left(\frac{dU_1}{dT}\right)_{v_m}$ must be negative. Now U_1 is the work spent per molecule against the molecular attraction in separating the molecules from one another by an infinite distance. This result therefore signifies that the attraction between two molecules separated by a constant distance decreases with increase of their temperature.

The Specific Heat at Constant Volume.

The quantities U_1 and u_1 are intimately connected with the specific heat at constant volume of a substance. The connection between them can be obtained by passing the substance through a closed cycle and equating to zero the total change in internal energy. Let S_v denote the specific heat in ergs at constant

volume of a gram of substance. Then if its temperature is raised by dT, keeping the volume constant, the amount of heat supplied is $S_v . dT$. Let the substance now expand, keeping its temperature constant, till its volume is infinitely great, and let $L_1 + dL_1$ denote the amount of heat supplied which represents the internal work done. On lowering the temperature of the gas by dT, keeping its volume constant, the heat given out is $-S_g . dT$, where S_g denotes the specific heat at constant volume of a substance in the state of a perfect gas. Experiment shows that S_g is independent of the volume of the gas, or $\frac{dS_g}{dv} = 0$. Next let the gas be compressed, keeping the temperature constant, till it occupies its original volume. Let $-L_1$ denote the heat given out during the process due to the internal work done. Equating the sum of the changes in internal energy to zero we have

$$S_v . dT + L_1 + dL_1 - S_g . dT - L_1 = 0,$$

or
$$\left(\frac{dL_1}{dT}\right)_{v_m} = S_g - S_v \quad \ldots\ldots\ldots\ldots\ldots\ldots(6).$$

Since
$$L_1 = \frac{1}{m_a}(U_1 + u_1 - u_a)$$

and
$$S_g = \frac{1}{m_a}\left\{\left(\frac{du_a}{dT}\right)_{v_m} + \frac{3Rm_H}{2}\right\},$$

the above equation may be written

$$S_v = \frac{1}{m_a}\left\{2\left(\frac{du_a}{dT}\right)_{v_m} + \frac{3Rm_H}{2} - \left(\frac{dU_1}{dT}\right)_{v_m} - \left(\frac{du_1}{dT}\right)_{v_m}\right\} \quad \ldots(7).$$

Let us suppose as before that $\left(\frac{du_1}{dT}\right)_{v_m} = \left(\frac{du_a}{dT}\right)_{v_m}$. The equation then becomes $S_v = S_g - \frac{1}{m_a}\left(\frac{dU_1}{dT}\right)_{v_m}$. Now S_v of a substance usually increases with its density, if it does not obey the laws of a perfect gas. This is shown in Table III which contains the

Table III.

ρ	S_v	ρ	S_v
·0377	·1714	·1177	·1942
·0554	·1778	·1238	·1963
·0635	·1799	·1323	·1992
·0891	·1869	·1444	·2030

values of S_v in grm cal. obtained by Joly* for CO_2 at different densities. S_g in grm cal. is equal to ·1601 and $S_v - S_g$ is therefore positive, and consequently $\left(\frac{dU_1}{dT}\right)_{v_m}$ must be negative. This result shows as before that the attraction between two molecules, on the above assumption, decreases with increase of temperature.

The Specific Heat at Constant Pressure.

An expression for the specific heat at constant pressure of a gram of substance can be found along the same lines as that at constant volume. It will be easily seen on passing the substance through a similar cycle as indicated in the previous section that the internal work done when the temperature of a gram of substance is increased by dT, keeping the pressure constant, which we will denote by S_{pi}, is given by equation (6) on substituting S_{pi} for S_v and $\left(\frac{dL_1}{dT}\right)_p$ for $\left(\frac{dL_1}{dT}\right)_{v_m}$. The specific heat at the constant pressure p is then given by

$$S_p = S_{pi} + p\left(\frac{dv}{dT}\right)_p = S_g - \left(\frac{dL_1}{dT}\right)_p + p\left(\frac{dv}{dT}\right)_p,$$

where $p\left(\frac{dv}{dT}\right)_p$ is the external work done during expansion by the substance. Now

$$L_1 = \frac{1}{m_a}(U_1 + u_1 - u_a),$$

and

$$S_g = \frac{1}{m_a}\left\{\left(\frac{du_a}{dT}\right)_{v_m} + \frac{3m_H R}{2}\right\},$$

further $\left(\frac{du_a}{dT}\right)_p = \left(\frac{du_a}{dT}\right)_{v_m} + m_a p\left(\frac{dv}{dT}\right)_p = \left(\frac{du_a}{dT}\right)_{v_m} + Rm_H$

since $m_a p\left(\frac{dv}{dT}\right)_p$ from the equation $pv = \frac{RT}{m}$ of a perfect gas is equal to Rm_H, where m is the molecular weight relative to hydrogen. The above equation giving S_p may now be written

$$S_p = \frac{1}{m_a}\left\{2\left(\frac{du_a}{dT}\right)_{v_m} + \frac{5m_H R}{2} - \left(\frac{dU_1}{dT}\right)_p - \left(\frac{du_1}{dT}\right)_p\right\} + p\left(\frac{dv}{dT}\right)_p \ldots(8).$$

The difference between the specific heat at constant pressure and that at constant volume is given by the equation

$$S_p - S_v = \frac{1}{m_a}\left\{Rm_H - \left(\frac{dU_1}{dT}\right)_p - \left(\frac{du_1}{dT}\right)_p + \left(\frac{dU_1}{dT}\right)_{v_m} + \left(\frac{du_1}{dT}\right)_{v_m}\right\} + p\left(\frac{dv}{dT}\right)_p \ldots(9).$$

* *Proc. Roy. Soc.* LV. p. 390, 1894.

When the substance is in the form of a perfect gas we have $U_1 = 0$, $\left(\frac{dU_1}{dT}\right)_p = 0$, and $\left(\frac{dU_1}{dT}\right)_{v_m} = 0$. Further

$$\left(\frac{du_1}{dT}\right)_{v_m} = \left(\frac{du_a}{dT}\right)_{v_m}, \quad \left(\frac{du_1}{dT}\right)_p = \left(\frac{du_a}{dT}\right)_p = \left(\frac{du_a}{dT}\right)_{v_m} + Rm_H$$

and $p\left(\frac{dv}{dT}\right) = \frac{R}{m}$. Equation (9) then becomes $S_p - S_v = \frac{R}{m}$.

The Specific Heat of a Liquid.

The methods that have been employed to measure the specific heat of a liquid give more or less exactly the specific heat at constant pressure. At low temperatures the external work done by the liquid on expanding with rise of temperature is small in comparison with the internal work done, but at high temperatures (near the critical point) this is no longer the case. Let us consider the quantity S_{pi}, the internal specific heat of a gram of substance at constant pressure. It is given by the equation

$$S_{pi} = S_g - \left(\frac{dL_1}{dT}\right)_p,$$

where L_1 denotes the internal heat of evaporation of a substance into a vacuum, and S_g its specific heat at constant volume when in the state of a perfect gas. The quantity $\left(\frac{dL_1}{dT}\right)_p$ has not yet been measured for any substance. It can be connected with the quantity $\frac{dL_1}{dT}$, for we have $\frac{dL_1}{dT} = \left(\frac{dL_1}{dT}\right)_p + \left(\frac{dL_1}{dp}\right)_T \frac{dp}{dT}$. Further $L = L_1 - L_2$, and hence $\frac{dL}{dT} = \frac{dL_1}{dT} - \frac{dL_2}{dT}$, where L denotes the internal heat of evaporation of the substance, and L_1 and L_2 the internal work done in separating the molecules by an infinite distance from one another of a gram of liquid and saturated vapour respectively. The quantities $\frac{dL}{dT}$, $\frac{dL_1}{dT}$, and $-\frac{dL_2}{dT}$, occurring in the last equation, are all negative, and it follows therefore that $\frac{dL}{dT}$ is numerically larger than $\frac{dL_1}{dT}$. Further the quantity $\left(\frac{dL_1}{dp}\right)_T \frac{dp}{dT}$ is positive, and therefore $\frac{dL_1}{dT}$ is larger than $\left(\frac{dL_1}{dT}\right)_p$ according to the second last equation; and consequently $\frac{dL}{dT}$ is larger than $\left(\frac{dL_1}{dT}\right)_p$. It follows therefore that if the former

quantity is used instead of the latter in the equation giving S_{pi}, the values obtained for S_{pi} should be larger than those found in practice. This was found to be the case, even at low temperatures. It is necessary therefore to discover an empirical expression for

$$\left(\frac{dL_1}{dT}\right)_p.$$

It was found that its value is approximately equal to $\frac{dL_1}{dT}$, if L_1 is calculated on the supposition that the work done in separating the molecules of a quantity of matter by an infinite distance from one another is entirely expended in overcoming the attraction between the molecules, and that the law of molecular attraction is that given by the writer in a previous paper*, viz.

$$\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right)\frac{(\Sigma\sqrt{m_1})^2}{z^5},$$

supposing $\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right)$, which for brevity we will always denote by (ϕ), is equal to a constant b. We have then† $L_1 = ba\,\frac{\rho_1^{\frac{4}{3}}}{m^{\frac{7}{3}}}(\Sigma\sqrt{m_1})^2$, and

$$L = L_1 - L_2 = ba\,\{\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}}\}\,\frac{(\sqrt{m_1})^2}{m^{\frac{7}{3}}},$$

where ρ_2 denotes the density of the saturated vapour and ρ_1 that of the liquid, and a a numerical constant. Therefore

$$\frac{dL_1}{dT} = \frac{4ba}{3}\rho_1^{\frac{1}{3}}\cdot\frac{d\rho_1}{dT}\cdot\frac{(\Sigma\sqrt{m_1})^2}{m^{\frac{7}{3}}} = \frac{L}{\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}}}\,\frac{4}{3}\rho_1^{\frac{1}{3}}\cdot\frac{d\rho_1}{dT},$$

on eliminating $\frac{(\sqrt{m_1})^2}{m^{\frac{7}{3}}}\,ba$, and consequently

$$S_{pi} = S_g - \frac{L}{\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}}}\,\frac{4\rho_1^{\frac{1}{3}}}{3}\cdot\frac{d\rho_1}{dT} \qquad \text{.....(10).}$$

This equation is tested in Table IV. The values of S_{pi} for CO_2 are taken from a paper by Dieterici‡, who calculated them from the results of his experimental investigations. The values for the remaining substances are taken from *Landolt and Börnstein's Tables*, 2nd ed. They correspond to temperatures for which $S_{pi} = S_p$. The values of S_g were also obtained from

* *Phil. Mag.*, Jan., 1911, p. 97 ; and previous papers.
† *Phil. Mag.*, May, 1910, pp. 789–795.
‡ *Annalen der Phys.*, Vol. XII., pp. 170–171 (1903).

TABLE IV.

t	ρ_1	$-\frac{d\rho_1}{dT}$	ρ_2	L cal. per grm.	S_{pi} experimental	S_{pi} calculated
Sulphur dioxide. $S_g = \cdot1223$						
0	1·435	·0025	·0045	83·56	·317	·316
40	1·325	·00285	·0181	70·73	·342	·325
120	1·018	·0055	·1255	44·29	·457	·462
140	·878	·00887	·216	32·67	·568	·579
145	·827	·01175	·254	28·57	·845	·805
153	·694	·0202	·3776	15·55	1·035	1·207
Ether. $S_g = \cdot454$						
0	·7362	·00114	$\cdot0_3827$	86·16	·529	·632
30	·7019	·00121	·002667	77·92	·547	·633
80	·6402	·00141	·01155	65·85	·690	·648
120	·5764	·00176	02934	54·91	·803	·682
140	·5385	·00210	·04488	48·31	·822	·714
180	·4268	·00497	·1135	27·09	1·041	·961
Carbon dioxide. $S_g = \cdot1601$						
0	·9139	·00409	·004091	48·36	·495	·466
5	·8882	·00582	·005821	44·46	·552	·554
15	·8137	·00901	·009010	34·50	·691	·731
20	·7660	·01064	·01064	29·78	·806	·814
25	·7033	·01378	·01378	22·07	·948	·917
27	·6711	·01800	·01800	17·00	1·105	1·02
28	·6527	·02087	·02087	14·00	1·205	1·05
29	·6299	·02818	·02818	12·40	1·48	1·10
30	·5981	·05047	·03047	8·85	1·85	2·00
Carbon disulphide $S_g = \cdot1312$						
0	1·2921	·00146	$\cdot0_35662$	82·76	·2352	·256
30	1·2473	·00150	·001759	78·97	·2401	·258
80	1·1684	·00163	·007473	71·03	·260	·263
120	1·0997	·00183	·01821	63·24	·276	·271
160	1·0216	·00201	·0369	54·28	·2882	·274

these tables. Both S_g and S_{pi} are expressed in cal. per grm. It will be seen that a fair agreement between calculation and experiment is obtained.

The Temperature Effect of U_1.

In a previous paper* we have brought forward some evidence from latent heat and surface tension considerations that the attraction between two molecules is a function of their temperature. In the reasoning $(u_1 - u_2)$ was supposed to be small in comparison with $(U_1 - U_2)$ in the case of latent heat of evaporation, for the truth of which there is some evidence. The surface tension, we have seen, is not affected by the quantity u_1. But it is probably affected by the surface transition layer, of which the mathematical investigation takes no account. It is of importance therefore that the point in question be investigated in as many ways as possible. It has already been considered in previous parts of this paper.

The thermodynamical equation $\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v$, according to what has gone before, may be written

$$\frac{1}{m_a}\left\{\left(\frac{dU_1}{dv_m}\right)_T + \left(\frac{du_1}{dv_m}\right)_T\right\} = T\left(\frac{dp}{dT}\right)_v - p.$$

Let us assume that $\left(\frac{du_1}{dv_m}\right)_T$ is small in comparison with $\left(\frac{dU_1}{dv_m}\right)_T$. Now U_1 is the energy necessary per molecule to separate the molecules of a substance by an infinite distance from one another. Therefore if the attraction is independent of the temperature the quantity $\left(\frac{dU_1}{dv_m}\right)_T$, or the right-hand side of the above equation, should be independent of the temperature for a constant value of v. Table V contains values of this quantity calculated by means of the above equation for CO_2 at different temperatures corresponding to the relative volumes ·001 and ·005. The data was obtained from *Landolt and Börnstein's Tables*, 1st ed. It will be seen that it is by no means constant for a constant value of v, but decreases in value with increase of temperature. This indicates that with a rise of temperature the attraction between two molecules decreases. It will be seen from the table that the decrease in the value of $\left(\frac{dU_1}{dv}\right)_T$ when the temperature is increased from 31° to 40° is less when the value of v is ·005 than when it is ·001. This would indicate that the greater the distance between

* *Phil. Mag.*, Jan. 1911, pp. 91–95.

two molecules the less is their attraction upon one another affected by the temperature.

TABLE V.

T	p	$\frac{dp}{dT}$	$-\left(T\frac{dp}{dT}-p\right)$
$v=\cdot001$			
313	5641·25	28·97	3426
304	5375·11	33·33	4765
$v=\cdot005$			
313	90·463	1·487	375
304	76·936	1·518	384

To test whether the undermentioned function $\phi\left(\frac{T}{T_c}, \frac{x_c}{z}\right)$ in the law of molecular attraction contains z the distance of separation of the molecules besides T the temperature, we will use the thermodynamical equation $\left(\frac{dQ}{dp}\right)_T = T\left(\frac{dv}{dT}\right)_p$. This equation may be written

$$\left\{\left(\frac{dU_1}{dv_m}\right)_T + \left(\frac{du_1}{dv_m}\right)_T\right\}\frac{1}{m_a} + p = -\frac{T\alpha}{\beta}, \text{ (equation 3),}$$

which becomes $$\frac{1}{m_a}\left(\frac{dU_1}{dv_m}\right)_T + p = -\left(\frac{T\alpha}{\beta}\right),$$

on neglecting $\left(\frac{du_1}{dv_m}\right)_T$ in comparison with $\left(\frac{dU_1}{dv_m}\right)_T$. Let us assume that the above function does not contain z. We obtain then

$$\frac{U_1}{m_a} = \frac{B\rho_1^{\frac{4}{3}}}{m^{\frac{7}{3}}}(\Sigma\sqrt{m_1})^2,$$

and $$L = U_1 - U_2 = B(\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}})\frac{(\Sigma\sqrt{m_1})^2}{m^{\frac{7}{3}}},$$

in the same way as the values of L_1 and L were obtained in the

section on the specific heat of a liquid, supposing the above equation to apply to a liquid in contact with its saturated vapour.

Therefore $$\frac{1}{m_a}\left(\frac{dU_1}{dv_m}\right)_T = \frac{cL}{\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}}} \frac{4}{3} \rho_1^{\frac{7}{3}},$$

where c is a numerical constant which should be equal to unity.

The above thermodynamical equation then becomes

$$\frac{L}{\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}}} \frac{4\rho_1^{\frac{7}{3}}}{3} \frac{\beta}{T\alpha} = -\frac{1}{c} \quad \text{.....(11).}$$

According to this equation the expression on the left-hand side should be independent of the temperature and nature of the liquid and equal to -1. The value of this expression or $-1/c$ is given in Table VI for a number of liquids at different temperatures. It will be seen that it is not constant, nor equal to unity, and that the above function in the law of molecular attraction must therefore contain z. The deviations from constancy are however small, and it may therefore as a first approximation be taken a function of the temperature only.

TABLE VI.

Ether		Benzene	
t	$-1/c$	t	$-1/c$
13·5	1·25	6	1·18
25·4	1·26	10	1·14
63	1·28	50	1·01
99	1·33		
78·5	1·51	Ethyl Acetate	
		13·3	1·26
		99·6	1·32

Joule-Thomson Effect.

The function (ϕ) in the law of molecular attraction, on which U_1 depends, may possibly consist of a number of positive and negative terms. This point has already been discussed in a

previous paper*. We are now in a position to make some important changes and additions.

This form of the function would indicate that the attraction between two molecules is the resultant of a number of attractions and repulsions which act independently. The force between two molecules would in that case pass through zero and change in sign for certain distances z of separation. These values of z are given by $\phi\left(\frac{T}{T_c}, \frac{x_c}{z}\right) = 0$, where T_c denotes the absolute critical temperature and x_c the distance of separation of the molecules in the critical state. From the form of (ϕ) it follows that for pairs of molecules at corresponding temperatures these distances are the same multiple or fraction of the distances of separation of the molecules in the critical state.

This property of the function can be experimentally investigated by allowing a mass of gas to expand from the density ρ_3 to ρ_4 over a large range of values of ρ_3 and ρ_4, without allowing it to do external work, and measuring the heating or cooling effect produced. The amount of heat L_5 that is absorbed or given out when unit mass of a substance expands between given limits of densities is according to the first section of this paper given by $L_5 = (U_3 - U_4 + u_3 - u_4)\frac{1}{m_a}$, where the suffixes 3 and 4 refer to the matter at the densities ρ_3 and ρ_4 respectively. If the expansion takes place adiabatically and without external work being done the heating or cooling effect is approximately given by $\frac{L_5}{S_v}$, where S_v denotes the average specific heat at constant volume.

In previous investigations (on latent heat of evaporation, etc.) we have neglected $(u_3 - u_4)$ in comparison with $(U_3 - U_4)$, and the results obtained have justified this assumption. The above equation may then, on making the same assumption, be written

$$\left\{\psi_3\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_3}\right)\cdot\rho_3^{\frac{4}{3}} - \psi_4\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_4}\right)\cdot\rho_4^{\frac{4}{3}}\right\}\frac{(\Sigma\sqrt{m_1})^2}{m^{\frac{1}{3}}} = L_5 \ldots (12),$$

on evaluating U_3 and U_4 from the general law of molecular attraction† in the same way as the value of L_1 in the section on specific heat of liquids, where $\Sigma\sqrt{m_1}$ denotes the sum of the square roots of the atomic weights of the atoms of a molecule. It follows from this equation that the Joule-Thomson effect of gases at corresponding temperatures when the initial and final densities during expansion are corresponding densities is proportional to $\frac{\rho_c^{\frac{4}{3}}(\Sigma\sqrt{m_1})^2}{S_v m^{\frac{1}{3}}}$. A heating effect indicates that over some range of

* *Phil. Mag.*, Jan. 1911, pp. 96–97.
† *Loc. cit.*

distance of separation of the molecules lying between their initial and final distance of separation during expansion the molecules repel one another, and a cooling effect indicates that they attract one another. Now experiment has shown that both a heating and cooling effect can be obtained. It follows therefore that the function (ϕ) consists of a number of positive and negative terms.

The points of inversion of a gas, that is for which there is no heating or cooling effect for a small expansion, are given by the equation $L_5 = 0$ or

$$\psi_3\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_3}\right) = \left(\frac{\rho_4}{\rho_3}\right)^{\frac{4}{3}} \cdot \psi_4\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_4}\right) \quad \ldots\ldots\ldots\ldots(13),$$

where $\rho_4 = \rho_3 + \delta\rho_3$, and taking the limiting form of the equation on putting $\delta\rho_3 = 0$. The equation reduces to the form

$$\psi_5\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_3}\right) = 0.$$

It follows from this equation that the point of inversion depends on the density as well as the temperature of the substance. Further, if a number of substances have corresponding densities their points of inversion will occur at corresponding temperatures. This condition has probably been approximately satisfied in experiments on the subject, since gases with a low critical temperature were found to have a low temperature of inversion.

It has been found that the cooling effect obtained with gases can be approximately represented by the expression $\frac{dT}{dp} = \frac{\alpha}{T^2}$, where $\frac{dT}{dp}$ is the change in temperature of the gas per unit change in pressure during expansion, and α is a constant which depends on the nature of the gas. But obviously this equation can only have a very limited range of application. When a gas is allowed to expand at different temperatures so that the initial and final volumes are always the same, and it behaves approximately as a perfect gas, that is obeys the law $pv = \frac{RT}{m}$, dp is proportional to T. The cooling effect is then from the above equation approximately inversely proportional to the temperature. But if the initial and final volumes during expansion of a gas at different temperatures are always the same, and the molecular attraction is independent of the temperature the cooling effect must also be independent of the temperature. Since it represents the energy expended in separating the molecules against their attraction, and under the above conditions is approximately inversely proportional to the temperature, it follows that the molecular attraction decreases with increase of temperature.

It is possible to find a value for α in the equation $\frac{dT}{dp} = \frac{\alpha}{T^2}$ in terms of some of the fundamental quantities of a substance. Let us suppose that the experiments on the Joule-Thomson effect of various gases are so carried out that their temperatures and initial and final densities during expansion are corresponding quantities. Let us further suppose that the gases obey approximately the law $p = \frac{RT\rho}{m}$ applying to a perfect gas. We have then that $dp = p_1 - p_2 = \frac{RT}{m}(\rho_1 - \rho_2)$, and the above equation may be written $dT = \frac{k_1 \alpha \rho_c}{T_c m}$, where k_1 is a quantity which is the same for all gases since they are at corresponding states, and ρ_c and T_c denote the critical density and temperature respectively. Now we have seen in an earlier part of this section that if the experiments are carried out under the conditions stated above the cooling effect is given by $\frac{k_2 \rho_c^{\frac{4}{3}}}{S_v m^{\frac{7}{3}}}(\Sigma\sqrt{m_1})^2$, where k_2 is the same for all substances. Equating these two expressions for the cooling effect we obtain $\alpha = \frac{k_3 \rho_c^{\frac{1}{3}} T_c}{S_v m^{\frac{4}{3}}}(\Sigma\sqrt{m_1})^2$, where $k_3 = \frac{k_2}{k_1}$ is an absolute constant since α is taken independent of the temperature and density of the gas.

It will be of interest to compare the value of this expression for α with that obtained by experiment. Joule has shown that at a temperature of 17° α has the value ·265 for air and 1·05 for carbon dioxide. Now in the case of carbon dioxide we have $\rho_c = ·464$, $T_c = 304$, and $S_v = ·1486$ at 17°; and in the case of nitrogen (principal constituent of air) we have $\rho_c = ·37$, $T_c = 127$, and $S_v = ·1735$. Putting k_3 equal to $7·544 \times 10^{-4}$ we obtain $\alpha = 1·03$ for carbon dioxide, and $\alpha = ·262$ for air. The agreement between calculation and experiment is thus very good.

Remarks.

In the previous sections we have shown that the internal energy of a substance can be divided into three parts, viz. U_1, u_1, and $\frac{3Rm_H T}{2}$. Various formulae involving these parts have been deduced.

In previous papers we have neglected $(u_1 - u_2)$ in comparison

with $(U_1 - U_2)$ when dealing with the internal heat of evaporation, and obtained a form for the law of molecular attraction which agrees with that deduced from the surface tension, though the latter quantity does not involve u_1. The rate of diffusion of gases, which does not involve u_1, could also be deduced from the law. It was then possible to deduce that the molecular attraction decreases with increase of temperature. These results fit in with the investigations in this paper.

If $(u_1 - u_2)$ is small in comparison with $(U_1 - U_2)$, for which there is considerable evidence, it is very likely that $\left(\frac{du_1}{dv_m}\right)_T = 0$, and $\left(\frac{du_1}{dT}\right)_{v_m} = \left(\frac{du_2}{dT}\right)_{v_m}$. Assuming this, we deduced in this paper that the molecular attraction decreases with increase of temperature, the same result as obtained on the first assumption. In the second part of this paper further evidence will be brought forward confirming this result.

The Chromosomes of a Giant form of Primula sinensis. By R. P. Gregory, M.A., St John's College. (Preliminary Note.)

[*Read* 26 February 1912.]

Giant races of *Primula sinensis* have been known in horticulture for some time. In an earlier communication *, the writer showed that in one of these Giant races, the individual cells and their nuclei are, on the average, larger than those in the ordinary (non-giant) type of *P. sinensis*, but the number of chromosomes is the same in both cases. In the course of a series of experiments with *P. sinensis*, a cross between two ordinary (non-giant) plants gave three very giant plants in the second generation. A further generation was raised by self-fertilizing one of these giant plants. The plants so obtained are all giants. An examination of one of them has shown it to possess distinctly larger nuclei than those of the ordinary type; and, although the material at present available for cytological examination does not permit of a precise statement as to the number of chromosomes, it is clear that the number in the meiotic divisions is greater than it is in the same divisions of the typical *P. sinensis*.

* *Proc. Camb. Phil. Soc.*, Vol. xv, p. 239, 1909.

PROCEEDINGS

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Cambridge Philosophical Society.

The Detection of Small Amounts of Polarisation in Light from a Dull Sky. By A. E. Oxley, M.Sc., B.A., Trinity College.

[*Received* 22 April 1912—*Read* 6 May 1912.]

If a polariscope, composed of a selenite plate and an analysing prism, be used to examine the light from a dull sky, the field of view is not appreciably coloured however the crystalline plate and the analyser are rotated with respect to each other and to any dissymmetry in the incident light. The proportion of polarised light is not large enough or the azimuth of the polarised vibration is too indefinite for it to be detected by this means. Probably both the smallness of the proportion of polarised light and the indefiniteness of the plane of polarisation are to be considered as effective in rendering the detection of polarised light from dull skies difficult.

The present paper contains an account of a method by which it is possible to detect such small amounts of polarisation as those which occur when dark clouds separate the observer from the open sky. In all cases the observations were conducted on a small region of the sky near the eastern horizon and the time of observation was sunset during the latter part of March and the early part of April.

Let us consider the fringes produced by plane polarised light from a bright sky when the light passes through a Babinet's compensator. The plane of polarisation is fairly well defined as can be seen by the sharpness of the change in tint produced in the bi-quartz when the latter is rotated through a small angle. When the sky is bright, coloured fringes are seen in the field of view and these are of maximum visibility when the principal direction of the analysing Nicol's prism is parallel or perpendicular to the direction of vibration of the incident polarised light.

When the sky becomes overcast the coloured fringes disappear, and however the compensator and analysing Nicol are rotated no fringes can be seen.

If this is the case, let a polarising rhomb be placed in front of the Babinet compensator so that the light from the sky first passes through it. Suppose a phase difference of $\frac{\pi}{2}$ is introduced between the components of each of the plane polarised vibrations which come from the part of the sky examined. It is found that for certain positions of the rhomb and compensator and the analysing Nicol the bands are made visible. The rhomb used was a bi-trapezoid* which produces a relative phase difference of $\frac{\pi}{2}$ over a wide range of wave length and admits of accurate adjustment with respect to the principal direction of the analysing Nicol. Moreover a rhomb of this form can be rotated without displacing the beam of light laterally. The arrangement of the apparatus is shown in fig. 1.

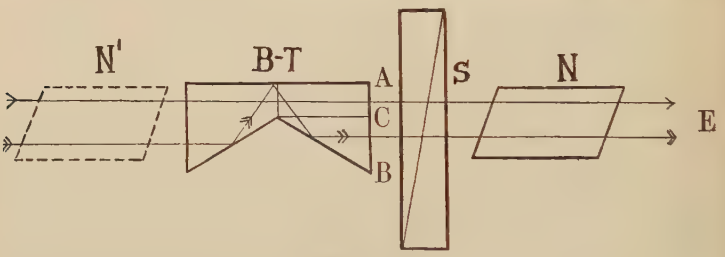


Fig. 1.

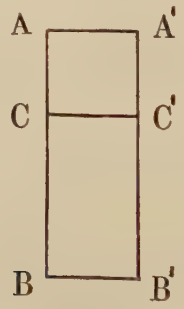


Fig. 2.

Here *BT* is the bi-trapezoid and *S* the compensator. On placing the eye at *E* the field of view is made up of the end view *ACBB'C'A'* (fig. 2) of the bi-trapezoid.

* A. E. Oxley, *Phil. Mag.* April, 1911, p. 517.

Over the portion $BCC'B'$ the light has been submitted to the action of the polariser, while the light which comes from the upper portion, $ACC'A'$, has passed directly through and has therefore not been influenced by the polariser. When the sky is dull the portion $ACC'A'$ of the field of view shows a uniformly grey illumination while $BCC'B'$ shows distinct dark bands. These bands terminate abruptly along the line CC' which is the image of the joint at the re-entrant angle of the bi-trapezoid. If a Nicol N' is placed in front of the bi-trapezoid, coloured bands stretch across the entire field of view, but the line CC' is a line of dis-

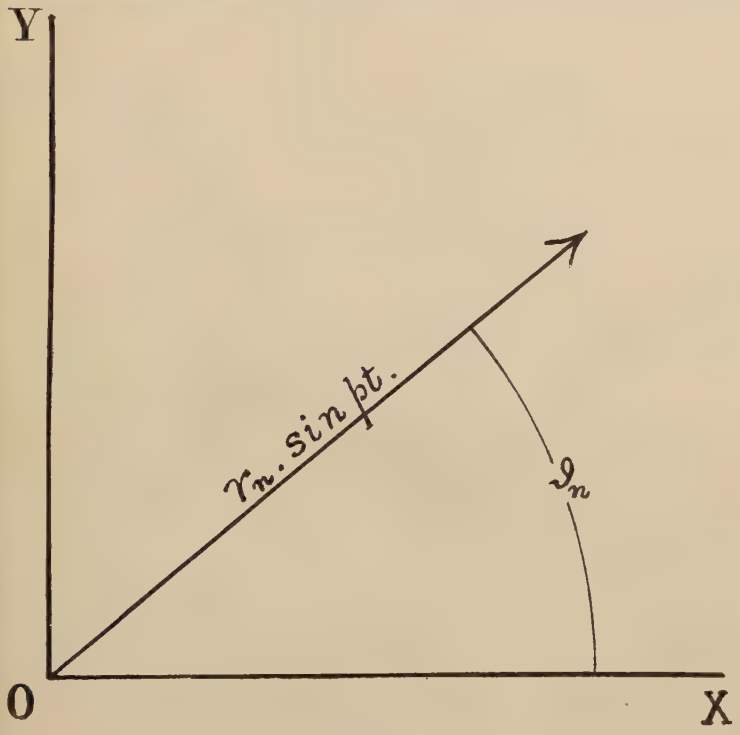


Fig. 3.

continuities, like a geological fault. On removing N' the bands in $ACC'A'$ disappear entirely and the bands in $BCC'B'$ remain, though their visibility is much reduced. These latter bands could be distinctly seen when, under the same conditions, no change of tint could be found on rotating various crystalline plates in the polariscope.

The effects observed are independent of the orientation of the bi-trapezoid with respect to the incident light. No bands could be seen in the area $BCC'B'$ when the edges of the bi-trapezoid

and compensator were parallel; the visibility of the bands was a maximum when the edges of the compensator and bi-trapezoid were inclined at an angle of 45°. When the principal direction of the Nicol's prism is parallel to a principal direction of the compensator (which is inclined at 45° to an edge of the bi-trapezoid) no bands are observed, but there is a maximum visibility of the bands when the principal direction of the Nicol is inclined at 45° to a principal direction of the compensator, *i.e.* parallel to an edge of the bi-trapezoid.

The increase in the visibility of the bands may be accounted for as follows:

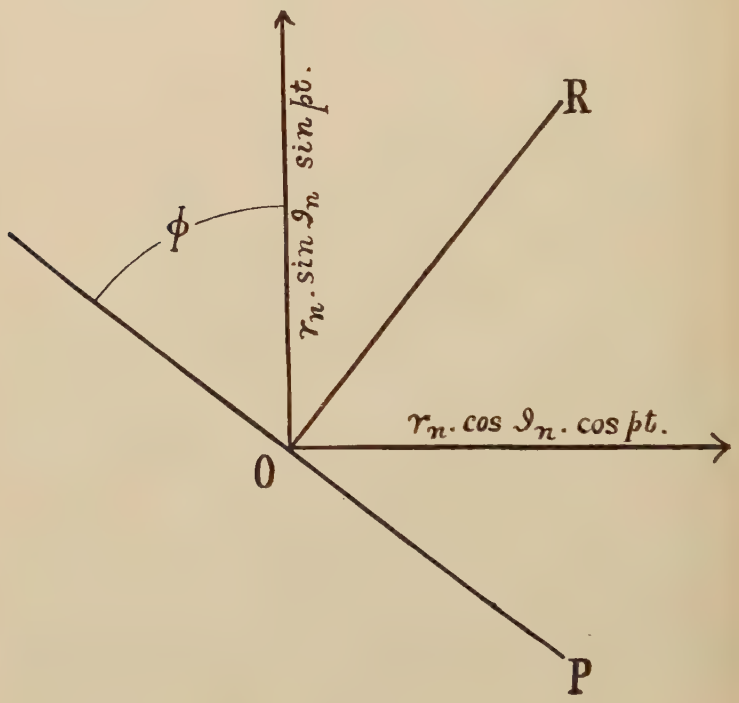


Fig. 4.

Let $r_n . \sin pt$ be an incident vibration inclined at azimuth ϑ_n with respect to an edge of the bi-trapezoid. The components of the vibration entering the bi-trapezoid are

$$r_n . \sin pt . \cos \vartheta_n, \text{ along } OX,$$
$$r_n . \sin pt . \sin \vartheta_n, \text{ along } OY.$$

The components leaving the bi-trapezoid are

$$r_n . \cos pt . \cos \vartheta_n, \text{ along } OX,$$
$$r_n . \sin pt . \sin \vartheta_n, \text{ along } OY.$$

Let ϕ be the angle between a principal direction of the compensator and a principal direction of the bi-trapezoid. The components entering the compensator along its principal directions are

$r_n . \sin\phi . \sin pt . \sin \vartheta_n + r_n . \cos\phi . \cos pt . \cos\vartheta_n$, along $OR \ldots A_n$ and

$r_n . \sin\phi . \cos pt . \cos\vartheta_n - r_n . \cos\phi . \sin pt \sin\vartheta_n$, along $OP \ldots B_n$.

Write $$\phi = \frac{\pi}{4} + \epsilon.$$

Then

$$A_n = \frac{r_n}{\sqrt{2}} \left\{ (\cos\epsilon + \sin\epsilon) . \sin pt \sin\vartheta_n + (\cos\epsilon - \sin\epsilon) \cos pt . \cos\vartheta_n \right\}$$

$$= \frac{r_n}{\sqrt{2}} \left\{ \cos\epsilon . \cos(pt - \vartheta_n) - \sin\epsilon . \cos(pt + \vartheta_n) \right\}.$$

Similarly

$$B_n = \frac{r_n}{\sqrt{2}} \left\{ \cos\epsilon . \cos(pt + \vartheta_n) + \sin\epsilon . \cos(pt - \vartheta_n) \right\}.$$

By experiment the visibility is best when $\phi = \frac{\pi}{4}$ and the above expressions show the effect of a slight variation, ϵ, from this value.

When $\epsilon = 0$, a condition maintained in all that follows,

$$A_n = \frac{r_n}{\sqrt{2}} . \cos(pt - \vartheta_n),$$

$$B_n = \frac{r_n}{\sqrt{2}} . \cos(pt + \vartheta_n).$$

Thus the amplitudes of the components along the principal directions of the compensator are equal and their phase difference is $2\vartheta_n$. This holds for all the components. Hence the resultant displacements along the principal directions of the compensator at any instant are

$$\overline{A} = \Sigma A_n = \sum_{n=1}^{N} \frac{r_n}{\sqrt{2}} . \cos(pt - \vartheta_n),$$

$$\overline{B} = \Sigma B_n = \sum_{n=1}^{N} \frac{r_n}{\sqrt{2}} . \cos(pt + \vartheta_n),$$

N being the number of plane polarised rays, a number whose magnitude is fixed by the smallest change in ϑ which it is necessary to distinguish.

Whatever be the value of the incident azimuth ϑ_n with respect to an edge of the bi-trapezoid, the direction of vibration of the light transmitted by the compensator is, for certain relative thicknesses of the quartz wedges, accurately inclined at an angle of 45° with

respect to a principal direction of the compensator, *i.e.* the direction of vibration of the light finally transmitted for certain relative thicknesses of the quartz wedges accurately parallel to an edge of the bi-trapezoid, and when the principal direction of the Nicol is perpendicular to this direction the bands are most visible. The positions of the centres of the bands are determined where the thicknesses of the quartz wedges are such that the phase difference produced by them, P (say), satisfies the relation

$$P + 2 . \overline{\Im} = 2n\pi,$$

where n is any integer and $\overline{\Im}$ is the mean azimuth of the incident vibration. The position of the Nicol which gives a maximum visibility to the bands is therefore theoretically accounted for. The increase in purity of the bands when this arrangement of apparatus is adopted appears to be due to the transference of a variation $\delta\Im$ in the azimuth of components in the incident vibration into a variation in phase difference $2\delta\Im$ in the compensator. Thus although for certain thicknesses of the quartz wedges the transmitted vibrations are accurately parallel to an edge of the bi-trapezoid, yet the vibrations are not accurately superposed but are slightly separated in the compensator by a distance representing a phase difference corresponding to twice the difference in azimuth which exists in the vibrations in the incident beam. Even when the direction of vibration of the incident light is sharply defined, as for example in the plane polarised vibrations produced by a Nicol's prism, the bands observed in the compensator are broad, the centre of the band being quite black and the illumination gradually increasing as we pass out. This is because the Nicol cuts out a great deal of the illumination due to the neighbouring eccentric ellipses. In the present case each plane polarised vibration is cut out by the Nicol, when properly placed, at those points of the compensator where the phase difference between its final components amounts to $2n\pi$, and in addition a great part of the illumination due to the neighbouring eccentric ellipses is stopped. If $\Im_n - \overline{\Im}$ is not very large, say a few degrees, then the vibrations eclipsed by the Nicol will be very nearly superposed and the effect of the superposition will be to produce dark bands which, unlike the Babinet bands, have no very black centre. If $\Im_n - \overline{\Im}$ is large, the superposition will give rise to fainter and more attenuated bands. This attenuation, which was slight, could be detected experimentally. The bands never acquire a high visibility owing to the fact that there is a large proportion of unpolarised white light present.

A pair of vibrations at azimuth $\Im + \delta\Im$ and $\Im - \delta\Im$ incident on the bi-trapezoid, and passing through the part of it marked $ACC'A'$, emerges from the compensator with components still

inclined at azimuth difference $2\delta\Im$ with respect to each other, and if the intensity of the incident light is small, the polarisation cannot be detected. When the sun is shining and the light from the sky is bright, coloured bands are seen in $ACC'A'$ as well as in $BCC'B'$, but the direction of vibration which gives rise to the bands in $ACC'A'$ is parallel to the original direction of vibration at incidence, as would be expected, while in $BCC'B'$ the direction of vibration is still parallel to one edge of the bi-trapezoid. Moreover the bands in $ACC'B'$, when they exist, are not continuous with those in $BCC'B'$, except under special conditions. Although the appearance of the bands in $ACC'A'$ is probably influenced by the increased brightness of the sky, still it seems that part of their brilliance is due to the existence of a more definite plane of polarisation when the brightness increases. The indefiniteness of the direction of the plane of polarisation, when the apparatus is directed towards a dull part of the sky, may be caused by the reflection of light, polarised in various azimuths, from brighter parts of the sky. When a bright sky is observed the amount of light so reflected is less important and the plane of polarisation is consequently more accurately defined. This, with the increase in intensity causes the appearance of bands in the region $ACC'A'$ of the field of view.

An arrangement of this type could be used as a direct reading polarisation chronometer and there would be no need to set the instrument each time the hour of the day was required. If $\overline{\Im}$ be the angle which the mean direction of vibration of the incident polarised light makes with an edge of the bi-trapezoid, then directing the instrument towards the pole the increase in $\overline{\Im}$ as the sun rotates is a true measure of change in solar time. Now keeping the wedges fixed the position of the central dark band at any instant is determined by the magnitude of $\overline{\Im}$. Hence the passage of the bands across the field of view is an indication of the elapse of solar time. If d be the distance between two bands, then the interval of time they represent is twelve hours and therefore in order that we may tell the hour of the day to within one minute of solar time, it will be necessary to distinguish $\frac{1}{720}$ of the distance between the bands. This may be possible if we use thin enough wedges in the compensator so as to increase d and if the light from the sky be moderately bright. The time could still be found even when the sky was so dull that the polarised light from it was not sufficient to give rise to complementary tints in a selenite or other crystalline plate, although of course to a much rougher approximation. In this respect and also on account of the greater accuracy attainable in the setting of the bi-trapezoid with respect to the compensator and analysing prism, the present form of polar chronometer will possess several additional advantages over the instrument devised by

Sir Charles Wheatstone*. The advantages of the latter instrument over the sun-dial are (1) there is no locality in which it cannot be used, whereas in the case of the sun-dial no object must intervene at any part of the day between the sun and the dial, (2) the instrument continues to indicate true solar time both before and after sunset and so long as an appreciable amount of the sun's rays are reflected from the atmosphere, (3) even when the sky is overcast, the instrument will continue to indicate the time providing the clouds are of small density. The accuracy attainable with a polar chronometer of the form described above is being investigated.

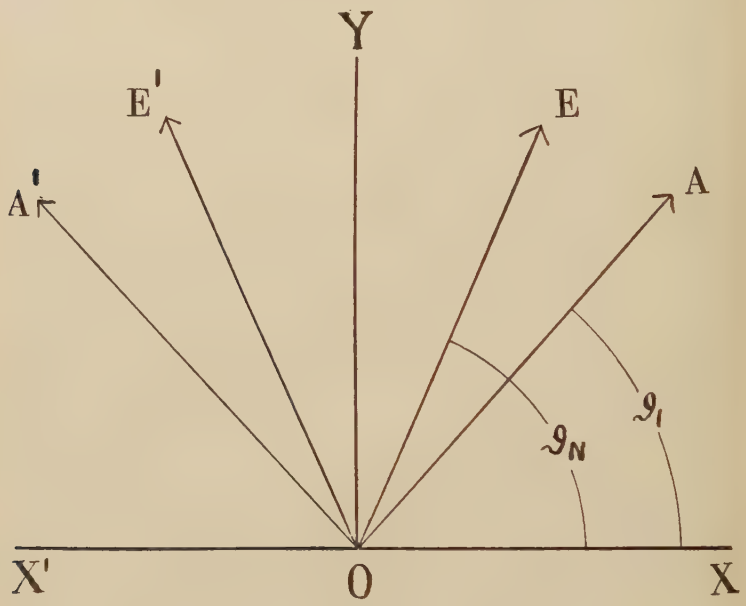


Fig. 5.

OA and *OE* are the extreme plane polarised vibrations in the incident light which pass through the bi-rhomb unaltered, the respective azimuths being ϑ_I and ϑ_N with regard to the principal direction *OX*. In the left half of the field the components of the incident vibrations parallel to *X'OX* have suffered a phase change of π and the transmitted plane polarised vibrations are represented by *OA'* and *OE'* at respective azimuths ϑ_I and ϑ_N with regard to *OX'*. Equality of illumination in the two halves of the field is obtained when the principal direction of the analysing Nicol is parallel to *X'OX*.

At the suggestion of Dr W. F. G. Swann, the efficiency of a half-wave plate in the detection of such small amounts of polarisation as are considered in this paper, was examined. Instead of using a half-wave plate, which produces between the transmitted

* *B. A. Report*, Swansea, 1848, p. 10.

components of a plane polarised vibration a phase difference of π for one particular wave-length only, a bi-rhomb* white light half-shade was used. If the polarisation from a dull sky can be detected by this means, the field of view when observed through a Nicol should be divided into two portions of unequal brightness, but there will be a position of the analysing Nicol for which the two halves of the field of view appear equally bright. This will occur when the principal direction of the Nicol is parallel to an edge of the rhomb forming the half-shade.

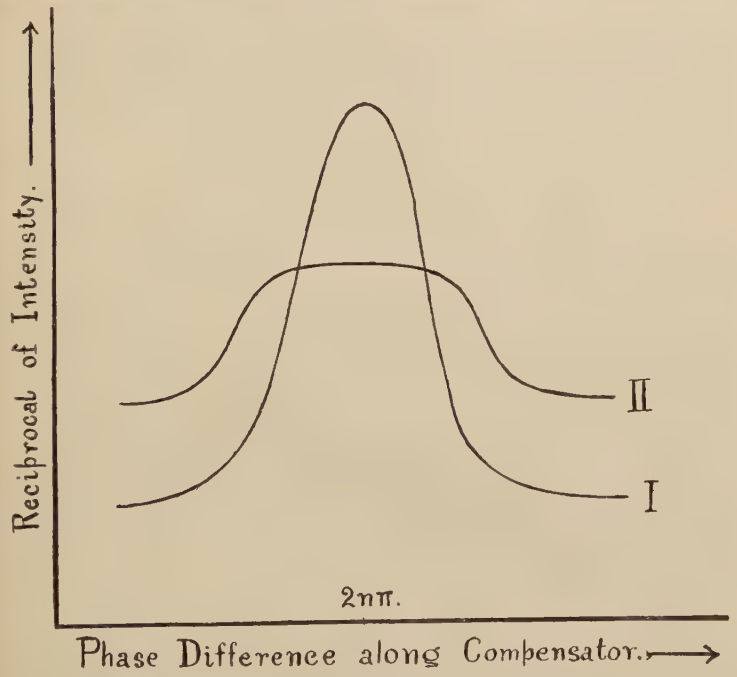


Fig. 6.

The existence of polarisation in light from a dull sky could be detected by this means when no tint could be distinguished in the bi-quartz. The method is not sensitive as the Nicol could be rotated through quite a large angle (25°), without any appreciable disturbance of the equality of the illuminations of the two halves of the field being detected. Further, this method does not locate the mean direction of the plane of polarisation. In the first arrangement in which the bi-trapezoid is used (fig. 1), a variation of the mean direction of the plane of polarisation with

* A. E. Oxley, *B. A. Report*, Sheffield, 1910, p. 536; *Chemical News*, Vol. CII., p. 190.

respect to an edge of the bi-trapezoid is accompanied by a displacement of the bands across the field of view of the compensator. If after any interval of time the central band has moved a measured distance, this distance corresponds to a phase difference in the compensator half the value of which is a measure of the angle through which the mean plane of polarisation of the incident beam has rotated in that interval. This method therefore not only indicates the existence of small amounts of polarisation but serves to determine the mean plane of polarisation of the incident light. The curves showing the relation between the reciprocal of the intensity of the light and the phase difference along the compensator are shown in fig. 6. Curve I is for light from a bright sky, curve II is for light from a dull sky.

It is hoped to continue this work on the polarisation of light from clouds.

Summary.

The existence of a small amount of polarisation in light from a dull sky can be detected by the method described, when no indication of it can be obtained by means of the tints produced in crystalline plates. The direction of the mean plane of polarisation can also be ascertained. After passing through the polarising rhomb and compensator, the plane polarised vibrations in the incident light give rise to bands in the field of view of the compensator which are like the Babinet bands when the sky is bright, but are slightly broader and fainter when the sky is dull. These faint bands can be distinctly seen when the amount of polarisation is not sufficient to produce visible complementary tints in a selenite plate. When the sky is dull, plane polarised vibrations of widely different azimuths, reflected from neighbouring parts of the sky, are of importance and these give rise to the slight attenuation of the bands.

I wish to record my indebtedness to Prof. W. M. Hicks, who for this investigation kindly placed the resources of the Physical Laboratory of the University of Sheffield at my disposal.

Note on the Action of Sunlight and of Radium Compounds on Glass. By W. A. Douglas Rudge, M.A., Professor of Physics, University College, Bloemfontein.

[*Read* 6 May 1912.]

It is probably well known that certain kinds of glass show a change in colour under the influence of ultra violet-light, Röntgen rays and radium emanations. The action of the first-named agent is very frequently brought to one's notice in tropical countries, especially in elevated situations, as fragments of glass are found which have been highly coloured. All kinds of glass are probably influenced, but it is only in the case of the common white glass, from which tumblers, etc. are made, that the effect is very noticeable, and in this case the effect is so marked that a piece of glass 4 cms. in thickness may become nearly opaque.

The writer has made some observations in order to find to what extent different kinds of glass were affected, and also if possible to make some kind of comparison with the rate and depth of colouration acquired by similar glass under the action of radium emanation.

The experiments were carried out on thick-walled tubing of different kinds of glass. Lengths of a few cms. were taken, control samples kept in a dark chamber and others exposed to sunlight, or partly filled with a radioactive material.

Experiments with sunlight.

The action of sunlight varied with the nature of the glass and in some cases the maximum colouration was attained with two months' exposure. A perceptible effect is seen in a few days, and if a colouration occurs the depth of it may be compared with that shown by a longer length of the control tubing if a simple darkening had occurred, but this could not be done if a change in the actual trial had taken place. In the latter case it generally happened that after two or three months had elapsed no further colouration went on, and if a pink colour was acquired its depth could be ascertained by comparison with a standard solution of potassium permanganate. The specimen of common glass shown, had probably been lying on the veldt for not more than three years.

Typical cases of colouration of glass tubing by sunlight.

Sept. 22nd. Exposed six pieces of glass tubing and rod to action of sunlight, control sampler being kept in the dark.

(1) Piece of ordinary soft tubing colour greenish.
(2) Barometer tubing colour pale grey green.
(3) Barometer tubing slight pink tint.
(4) Barometer tubing pale yellowish green.
(5) Glass rod nearly white.
(6) Jena hard glass tubing.

Oct. 7th.

(1) Had become darker in tint, about $\frac{6}{5}$.
(2) Slightly bleached.
(3) Colour changed in tint and darkened $\frac{3}{2}$.
(4) Colour changed to a dull pink.
(5) Colour changed to amethyst.
(6) No change.

Oct. 31st.

(1) Lighter than on Oct. 7th.
(2) „ „ „ bleached to original condition.
(3) Colour darker than on last occasion.
(4) „ „ „
(5) „ „ „
(6) No change.

Nov. 30th. No change since last observation.

(1) „ „ „ „
(2) „ „ „ „
(3) „ „ „ „
(4) „ „ „ „
(5) „ „ „ „

The action of radioactive material is very similar to that of sunlight; but it is much more intense as regards the final depth of colouration attained; it differs from sunlight in not (at first at all events) acting equally through the whole of the glass, but after several years the glass does become uniformly tinted. The rate of colouration* is not quite uniform, the innermost layer being more rapidly coloured than the outer layer, if, as is usually the case, the glass tube is not perfectly uniform throughout the substance of its walls.

The specimen shown indicates the result of the action of 3 centigrammes of a radioactive preparation stated to contain $\frac{1}{10000}$ of its weight of radium bromide and the action had been going on for about six months. The tubing used is the same as No. 4

* *Proceedings Roy. Soc. South Africa*, 1911.

of the samples submitted to sunlight. No comparison can be instituted between the two, but the action of the radium salt is much more intense than that of the sunlight.

I believe that the amethyst colouration produced by the action of sunlight and of radium on glass to be due to the presence of manganese in the glass. It may be objected that quartz is also coloured by radium, but in this case I think it is quite conceivable that the small amount of manganese necessary to give the colouration may naturally be present in the quartz. The colouration in the case of quartz is destroyed by heating, and this is also the case with the glass specimens.

A Negative Result on the Refraction of X-rays. By J. Crosby Chapman, B.Sc., Layton Research Scholar, University of London, King's College. Research Student, Gonville and Caius College, Cambridge. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 6 May 1912.]

This experiment gave a negative result when an attempt was made to refract X-rays by means of ethyl bromide vapour. It is one of many researches which have had the object of refraction in view. Most of these were carried out at a time when little was known of secondary and more especially homogeneous radiation. Owing to this it was thought advisable to try an experiment which would give more favourable conditions for obtaining evidence of refraction.

It has been shown by several experimenters* that any substance with atomic weight greater than 40, emits when suitably excited by X-rays, a definite characteristic radiation. It is in connection with this characteristic radiation that this research was made.

There are several hypotheses which have been brought forward to account for the fact that X-rays are not refracted by ordinary matter; one of these is that in all probability the X-ray pulse owing to its small diameter is incapable of affecting more than a single atom, at any one moment. This would seem to be a very legitimate theory. In this experiment, however, the conditions are exceptional in that the known characteristic radiation is stimulated, and with our present knowledge it is impossible to make any hypothesis concerning the action which takes place when a primary pulse causes a bromine atom to emit a characteristic radiation. It is quite reasonable to suppose that when the bromine is excited there will be exceptional relations existing between the various atoms in the neighbourhood of the main disturbance. So that bromine may serve to refract X-rays only when it is itself excited.

The two exceptional conditions under which it might be possible to detect refraction are as follows: (1) when the radiation which is to be tested as regards its refrangibility excites the radiation characteristic of the bromine vapour which is used as the prism: (2) when the radiation which it is attempted to refract in addition to merely exciting the characteristic radiation is

* Barkla and Sadler, *Phil. Mag.* Oct. 1908; Chapman, *Proc. Roy. Soc.* A, 1912, Vol. 86.

selectively absorbed by the bromine vapour. (1) will be referred to as general refraction since the whole range of radiation harder than the bromine characteristic radiation is capable of exciting the latter and therefore on this view would be capable of refraction. (2) will be referred to as anomalous dispersion since in this case something of the nature of a selective refraction is sought for.

Although in the course of this paper, terms such as refraction and dispersion are used, it is not meant by this that the analogy between light and X-rays is to be pressed. In fact several phenomena of X-rays, especially in connection with absorption, would indicate that there can be no close resemblance between light and Röntgen radiation.

The first part of the experiment is devoted to an attempt to detect general refraction; while the second part is an attempt to detect the presence of anomalous dispersion.

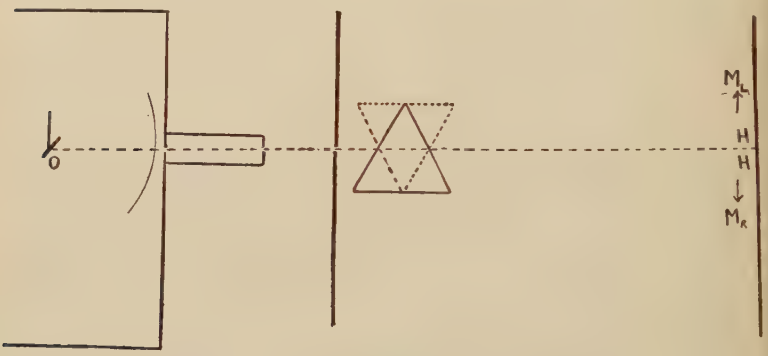
General Refraction.

In order to investigate whether there is any general refraction, a heterogeneous beam of X-rays was passed through a prism of ethyl bromide vapour. The bromine in this compound gave out an intense characteristic radiation* when excited by the primary beam used in this experiment.—The arrangement of the apparatus indicates the method adopted. Rays from an X-ray bulb at *O*, passed through three fine pin holes in lead screens placed a few centimetres apart in strict alignment with the anticathode. In this way an exceedingly narrow pencil of X-rays was obtained. The rays after leaving the screens passed through the prism *P* and eventually struck a photographic plate at *H*. The prism was made of brass with thin aluminium windows, constructed so as to be air-tight and the air inside was saturated with ethyl bromide at the temperature of the room. No rays struck the brass of which the prism was made.

The method used to detect general refraction was as follows. The photographic plate was placed in position at *H*. This plate moved in a horizontal slide so that any desired portion of its surface could be exposed to the rays. The bulb was then worked to the required degree of hardness and the prism placed in the position *R* (see figure). The bulb was then run for ten minutes, the rays which passed through the prism striking the plate for this period of time. The photographic plate was now moved horizontally so that a new portion came under the action of the X-rays. The prism remaining in the position *R*, the tube was

* Chapman, *Phil. Mag.* April 1911.

run for five minutes. At the end of this time keeping the plate in the same position, the prism was rotated into the position *L*. The bulb was again run for five minutes, thus the two exposures on the plate were both produced by rays acting over the same period of time. The reason of this method being used was that owing to the walls of the prism and ethyl bromide vapour scattering the primary X-rays, it was necessary to arrange so that the scattering, which in past experiments has caused great difficulty, should be the same in the two cases. It will be seen that *with the above arrangement this essential condition is obtained*: for owing to the narrowness of the pencil the path of the rays in the prism, if there is no refraction, is the same whichever position the latter occupies.



R = position of prism indicated by continuous line.
L = position of prism indicated by dotted lines.

Consider now the effect of the two exposures on the plate. Obviously if there is no refraction the two spots obtained should be of the same size for the rays have passed straight through the prism suffering the same absorption and scattering in the two cases and in addition the length of each total exposure is the same. Suppose however refraction takes place, when the prism is in the position *R*, any refraction that occurs will cause a shifting of the rays in the direction M_R. That is, the spot will be slightly wider in this case than if no refraction existed. When however the prism is placed in position *L*, there will be a shifting of the rays in the opposite direction towards M_L. So that in the latter exposure, which was given in two parts, we should get two spots, side by side or at least partially superposed. It is possible from the difference in their diameters to obtain a limiting value for the refractive index.

The results are given below in tabular form:

Angle of prism = 60°,

Vapour pressure of ethyl bromide = 257 mms.,

Length of path of rays in prism = 5 cms.

Distance from prism to plate = 30 cms.

Plate	Exposure	Position of Prism	Length of Exposure	Diameter of Spot
I	α	R	10 mins.	·241 cms.
,,	β	R	5 mins.	·247 cms.
		L	5 mins.	
II	α	L	10 mins.	·250 cms.
,,	β	R	5 mins.	·248 cms.
		L	5 mins.	
III	α	L	10 mins.	·243 cms.
,,	β	L	5 mins.	·257 cms.
		R	5 mins.	

Mean difference in diameter of spots (Double exposure − single exposure) $= (\beta - \alpha) =$ ·006 cms.

That is the difference is within the limits of experimental error, therefore within these limits

$$\mu = 0.$$

The conditions of the experiment would have been sufficient to detect a beam of rays the angle of refraction of which when passed through the prism

$$\delta = 0° 1' 0'',$$

that is assuming angle of incidence on prism = 30°, the following value of the refractive index could have been measured,

$$\mu = 1{\cdot}0003.$$

So that the result of this part of the experiment shows no general refraction by ethyl bromide vapour (even when its characteristic radiation is excited) by a method which if refraction had existed to such an extent that

$$\mu = 1{\cdot}0003,$$

the conditions of the experiment would have revealed its presence.

Anomalous Dispersion.

Closely connected with the emission of the characteristic radiation is the phenomenon of selective absorption* which elements exhibit for radiations which are just more penetrating than their own characteristic radiations. This fact led to the idea that in the neighbourhood of an absorption band it might be possible to detect anomalous dispersion and thence establish refraction even though it was impossible owing to the small magnitude of the effect to detect the normal refraction phenomenon.

The arrangement of the apparatus was similar to that in the first part of the experiment, though the method used was, for the sake of convenience, slightly modified. Heterogeneous X-rays direct from a Röntgen bulb served as the beam which it was attempted to refract abnormally. It might appear that it would have been more desirable to work with secondary homogeneous rays as the source, as in this case had anomalous refraction existed the whole beam on account of its homogeneity would have been refracted to the same extent. It will be seen however that it is much more desirable to use a heterogeneous primary, for apart from the fact that exposures of a day or more would have to be given when using the feeble secondary radiation in place of the primary beam, theoretical considerations show that the most likely type of radiation to suffer anomalous dispersion is that which is of such a degree of hardness that it is absorbed to a maximum extent by the ethyl bromide vapour. Had a homogeneous radiation been used, it would have been impossible owing to the comparatively few elements which emit characteristic radiations to select an element which just happened to emit a radiation which was absorbed to a maximum extent. When however a heterogeneous beam from an X-ray bulb is employed, there is in the radiation leaving the tube rays of varying degrees of hardness and if a suitable bulb is used it can be arranged that the radiation should contain rays of that order of penetrating power which is necessary for selective absorption in the ethyl bromide†. So that the heterogeneity of the rays is an advantage in that any type of radiation which can be anomalously refracted will be present in the primary beam and will separate itself from the main beam on leaving the prism. The X-ray bulb was fitted with a palladium side tube for softening so that it was possible to adjust the bulb so that the mean penetrating power of the heterogeneous rays was of any desired value.

Having shown in the first part of this experiment that there is no general refraction, it is possible with a single exposure of the plate to investigate whether there is any appreciable anomalous

* Barkla and Sadler, *Phil. Mag.* May, 1909; Chapman, *Proc. Roy. Soc.* A, Vol. LXXXVI. 1912.

† Barkla, *Phil. Mag.* Aug. 1910.

dispersion. This was done as follows: the prism was placed in the position R and the plate at H was exposed for ninety minutes. A long exposure was desirable owing to the fact that only a small constituent of the primary rays will suffer anomalous dispersion. It was not thought advisable to adopt the method used in the first part of the experiment as it was impossible to keep the bulb constant over a period of two hours even though intermittent runs were given. Had it been possible to keep the bulb constant for such long periods the two parts of the experiment could have been done at the same time. Of course had a large constituent of the primary beam been anomalously dispersed, the first part of the experiment would have detected it; the second part was performed in order to obtain a record on the plate even if only 2 % of the heterogeneous primary was of that degree of hardness necessary for selective dispersion. All previous experiments which tested the rays coming from a primary bulb show that with a bulb such as that used, a greater percentage of the rays than this would be in the region where selective absorption is obtained.

It will be seen that in the case of a single long exposure, if dispersion takes place, there should be obtained on the photographic plate the central spot corresponding to that constituent of the beam which the first experiment has shown is not refracted, and in addition to this and partially or wholly separated from it another spot or streak showing the position of the dispersed rays.

When this experiment was tried only the central spot was obtained and there was no trace of any other mark on the plate. Previous experiments had shown that if the whole of the primary rays fell on the photographic plate an appreciable effect was produced in thirty seconds. The method of the experiment would certainly have detected a dispersion of the rays corresponding to a refractive index

$$\mu = 1{\cdot}005.$$

That is when an attempt was made to detect an anomalous dispersion of X-rays, by a prism of ethyl bromide vapour, using a primary beam of that degree of hardness which is necessary for selective absorption, the experiment shows that 2 % of the total beam was not refracted to such an extent that

$$\mu = 1{\cdot}005.$$

Although this experiment has failed to show refraction, it seems advisable to publish it, in the form of a short note, as it would appear that it has been performed under the limiting conditions, and as this method has failed, attempts on the old lines, using prisms of scattering materials such as carbon, are quite out of the question.

I wish to thank Sir J. J. Thomson for his interest in this experiment.

The Structure and Homology of the Microsporidian Spore, as seen in Nosema apis. By H. B. Fantham, D.Sc. Lond., B.A., Christ's College, Cambridge, and Annie Porter, D.Sc. Lond., F.L.S., Quick Laboratory, Cambridge.

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I. Introduction.

During our investigation of the life-cycle of *Nosema apis*, the pathogenic agent of "Isle of Wight" disease in bees, a detailed study was made of the spore structure with the result that the complicated morphology of the minute spores of the parasite was elucidated. A short account of the structure of the spore of *N. apis* is given in this paper, followed by suggestions for homologising the structures seen.

II. Structure.

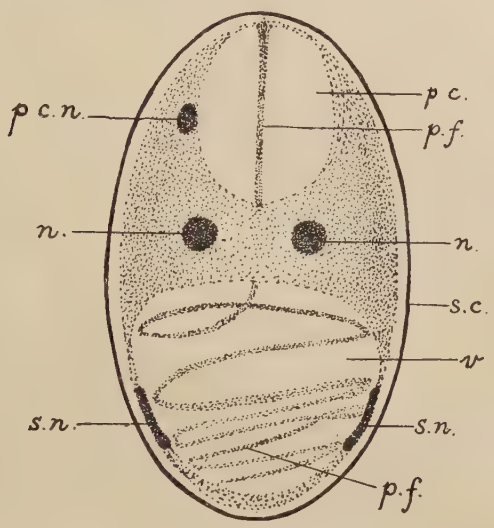
The mature spore of *Nosema apis* is, on the average, 5 μ by 2 μ in size. Despite its minuteness, it contains cytoplasm, a coiled thread that may reach 60 μ in length, and, according to its age and period of development, from one to five nuclei.

Each oval spore is enclosed in a highly resistant and ultimately opaque, firm membrane, the sporocyst (Fig. *s.c.*). The cytoplasm within the mature spore forms a median, peripheral girdle or ring known as the sporoplasm, leaving thus a vacuole at both poles of the spore. One vacuole usually is smaller than the other, and as the coiled thread mentioned previously is ejected through it for purposes of attachment of the spore to a host cell, it may be termed the anterior vacuole or polar capsule (Fig. *p.c.*). The larger vacuole, then, is posterior (Fig. *v.*). and is the more marked in a fresh, untreated spore. When the spore is treated with certain reagents, such as iodine water or dilute acetic acid, the long thread, formerly coiled up in the posterior vacuole, is seen to protrude from the smaller, anterior vacuole. The thread is the polar filament (Fig. *p.f.*), which, as it is concealed usually in life, and invisible in the mature spore until after treatment, is cryptocystic.

A spore is produced from a single, uninucleate mother cell, known as a pansporoblast or sporont; hence the pansporoblast is monosporous in *Nosema apis*.

The attainment of the quintinucleate condition of the spore of *Nosema apis* is the result of a series of divisions of the original, single nucleus, the process being as follows: The nucleus of the young spore divides into two similar nuclei by a process of division which might be termed amitotic, but is probably a sort of promitosis intermediate between mitosis and amitosis. From one of the daughter nuclei a small bud is given off, which passes to the polar capsule. The nucleus thus budded off is the polar capsule nucleus (Fig. *p.c.n.*). The remaining nucleus from the

original division divides into two small nuclei (Fig. *s.n.*), which gradually pass to the periphery. Their function appears to be that of controlling the secretion and growth of the sporocyst. Hence, considered from the point of view of their function, they are most appropriately termed the sporocyst nuclei (Fig. *s.n.*), though by homology with similar structures in *Myxosporidia*, the name of valvular or parietal nuclei is often applied to them. The sporocyst nuclei become elongate and thread-like, and closely applied to the peripheral cytoplasm of the spore. The remaining nucleus of the sporoplasm divides into two (Fig. *n.*) ultimately,



Spore of *Nosema apis*.

Slightly diagrammatic. As seen after long staining with Romanowsky solution.

p.c.	polar capsule or anterior vacuole.
v.	posterior vacuole.
n.	sporoplasmic nuclei.
s.n.	sporocyst (valvular or parietal) nuclei.
p.c.n.	polar capsule (capsulogenous) nucleus.
p.f.	polar filament.
s.c.	sporocyst.

and the mature spore then contains five nuclei arranged thus: a binucleate sporoplasm, the sporocyst nuclei at the periphery, and a polar capsule (capsulogenous) nucleus anteriorly. These five nuclei show slight variation in size and shape in different spores. They do not all persist in the spore for the same length of time, as the polar capsule nucleus and the two sporocyst nuclei gradually degenerate after fulfilling their function.

III. Homology.

If endeavour be made to compare the quintinucleate spore of a Microsporidian like *N. apis* with the spore of a Myxosporidian such as *Myxobolus*, similar elements are found to be present in the latter, though the numbers of each element may differ. *Myxobolus* has a sporoplasm (usually binucleate), two polar capsule cells which are present as definite cells, and two nucleated valvular cells. Each valvular cell gives rise to one of the valves of the bivalved spore.

When intermediate and annectant forms like *Coccomyxa* and *Telomyxa* are considered, the relationship is much more evident. *Coccomyxa morovi*, a parasite of the Sardine, is a monosporous Myxosporidian, whose single, bivalved spore contains a clearly visible, single polar capsule. Within the spore there is a binucleate sporoplasm, two nucleated valvular cells and one polar capsule cell. The structure of the spore of *Coccomyxa*, then, is strongly suggestive of that of *Nosema apis*. They are alike as regards the binucleate character of the sporoplasm, the sporocyst is formed under the influence of two sporocyst or valvular nuclei and the polar capsule is provided with a nucleus in each case. The sporocyst of *N. apis* is homologous with the bivalved shell or spore-membrane of *Coccomyxa*, and the comparison may be emphasised by the fact that in certain young spores of *N. apis* examined by us, a "line of weakness," more or less longitudinally disposed, has been found, though the mature spore of *N. apis* is never bivalved nor has it a sutural line. Such a line of weakness in *N. apis* spores may represent a transitory ancestral feature.

The polar capsule of *N. apis* is cryptocystic, that of *Coccomyxa morovi* is easily seen, as in most *Myxosporidia*, but in each case the polar capsule arises from a potential nucleated cell. *Coccomyxa*, then, is a Myxosporidian with certain marked Microsporidian characters, and as such, is a valuable link between the two groups.

Nor is evidence from the Microsporidian side of the close relationship between the two groups lacking. Recently a pathogenic Cnidosporidian from the fat body of the larva of *Ephemera vulgata* has been described under the name of *Telomyxa glugeiformis*. Internally, the spore of the parasite presents a definite Myxosporidian feature in that two polar capsules are present, but, on the other hand, it has the undoubted Microsporidian character that the polar capsules are cryptocystic. In addition, like *Nosema apis* spores, the *Telomyxa* spore shows two valvular nuclei, which are seen with difficulty even in stained preparations, but two polar capsule nuclei are present as in most *Myxosporidia*.

Coccomyxa and *Telomyxa* thus provide two bridges of the gap

existing between the *Myxosporidia* as exemplified by *Myxobolus*, and the *Microsporidia* as represented by *Nosema*.

Before concluding, we should like to refer to a recent paper on the *Sarcosporidia* by Crawley. The systematic position of the group Sarcosporidia is still somewhat uncertain, though they are usually considered to be related to the *Cnidosporidia*. In the spore of *Sarcocystis rileyi*, parasitic in ducks, Crawley found two vacuoles and two chromatin masses successively alternating with each other. The first (anterior) vacuole is probably homologous with the polar capsule of the *Cnidosporidia*, the first nucleus is compact and elongated and may be homologous with the parietal nuclei of the *Cnidosporidia* or possibly with the polar capsule nuclei—more probably with the compact parietal (somatic) nuclei. The second vacuole may be homologised with the posterior vacuole of various Microsporidian spores, while the second nucleus, which is vesicular, is probably homologous with the vesicular nuclei of the developing spores of *Myxobolus* or of *Paramyxa* and represents the nuclei of the sporoplasm, which may be germinal in character. Crawley has made no attempt to homologise the structures described by him in the spore of *Sarcocystis*, so we offer these suggestions in the hope that those having the opportunity to examine the very interesting group of the *Sarcosporidia*, will pursue the matter further.

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On the Different Kinds of Internal Energies of a Substance. II. By R. D. Kleeman, B.A., Emmanuel College, D.Sc. (Adelaide), Clerk Maxwell Student of the University of Cambridge.

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Molecular Attraction and the Radius of the Sphere of Action of a Molecule.

The radius of the sphere of action of a molecule in a gas is probably largely due to the field of force surrounding it. Information on this point can be obtained by comparing the radius deduced from viscosity data with that deduced from the density of the substance at the absolute zero. In the latter case the molecules have no motion of translation and are therefore in 'contact' with one another. The diameter σ_1 of the sphere of action from viscosity data is given* by the equation

$$\sigma_1^2 = \frac{\cdot 44 \rho V}{\eta \sqrt{2}\, \pi N},$$

where η denotes the coefficient of viscosity, N the number of molecules per c.c., ρ the density of the gas, and V the velocity of translation of a molecule. Denoting by m_a and m the absolute and relative masses of a molecule we have

$$N = \frac{\rho}{m_a}, \qquad V = \left(\frac{3RT}{m}\right)^{\frac{1}{2}},$$

where T denotes the temperature and R is the gas constant whose value is $8{\cdot}26 \times 10^7$, and the above equation may be written

$$\sigma_1^2 = \frac{2{\cdot}507 \times 10^{-21}}{\eta} \sqrt{Tm} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

The diameter σ_2 obtained from the density of the substance at the absolute zero may be taken to be approximately given by the equation

$$\sigma_2 = \left(\frac{m_a}{4\rho_c}\right)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2),$$

since according to Cailletet and Mathias' linear diameter law the density at the absolute zero is about four times the density ρ_c at the critical point.

If the molecules exert attraction upon one another for all distances of separation, we should expect that σ_1 is greater than σ_2. This is shown for two gases at zero temperature in Table I.

* Jeans, *Dynamical Theory of Gases*, p. 250.

TABLE I.

$t=0°$	$\frac{1}{2}\sigma_1$	$\frac{1}{2}\sigma_2$
Ether	$3{\cdot}59 \times 10^{-8}$ cm.	$2{\cdot}42 \times 10^{-8}$ cm.
Benzene	3·58 „	2·34 „

We should also expect that σ_1 depends on the temperature. An increase of temperature produces an increase in the velocity of translation of the molecules, and consequently the deflection of one molecule by another caused by their molecular attraction is on the average decreased. Hence the value of σ_1 should decrease with increase of temperature. This is shown in Table II for two substances at different temperatures.

TABLE II.

t	$\frac{\sigma_1}{2}$ for Benzene	t	$\frac{\sigma_1}{2}$ for Carbon dioxide
0	$3{\cdot}59 \times 10^{-8}$ cm.	0	$2{\cdot}94 \times 10^{-8}$ cm.
19	3·39 „	53·5	2·14 „
100	2·63 „	162·4	2·01 „

Since σ_1 decreases with increase of temperature, a temperature may exist for each substance which corresponds to $\sigma_1 = \sigma_2$, or even to $\sigma_1 < \sigma_2$. Two examples of σ_1 being less than σ_2 are given in Table III. This could not be the case if the force between two molecules is one of attraction for all distances of separation.

TABLE III.

$t=0°$	$\frac{1}{2}\sigma_1$	$\frac{1}{2}\sigma_2$
Carbon dioxide	$2{\cdot}21 \times 10^{-8}$ cm.	$2{\cdot}94 \times 10^{-8}$ cm.
Nitrous oxide	2·22 „	3·28 „

It appears therefore that for small distances of separation the force changes to repulsion. A region would then exist around a molecule through which another molecule might be able to pass, but which would not be occupied by matter when the molecules

are at rest at the absolute zero. The region of contact between two molecules would at that temperature be that where the force of attraction changes to repulsion. In a subsequent paper we shall obtain further evidence of the existence of this region.

The temperature at which σ_1 becomes equal to σ_2 is very likely a corresponding temperature. The values of σ_1 in Table III are calculated for temperatures much above the critical temperatures of the substances, and the values of σ_1 in Table I for temperatures much below the critical temperatures. If the temperatures in the latter case were the same multiple of the critical temperature as in the former, σ_1 would probably in this case also be less than σ_2.

That the diameter σ_1 of the sphere of action of a molecule probably obeys the law of corresponding states can be shown as follows. If it is principally due to the field of force surrounding the molecule it is approximately proportional to the distance of approach of two molecules at which their mutual potential and kinetic energies are equal to one another, this being the distance of approach at which the molecules do not separate again. The attraction of one molecule on another is given by

$$\phi\left(\frac{T}{T_c}, \frac{x_c}{z}\right)\frac{(\Sigma\sqrt{m_1})^2}{z^5} \text{ or } (\phi)\frac{(\Sigma\sqrt{m_1})^2}{z^5} \quad \ldots\ldots\ldots(3),$$

where z denotes the distance of separation of the molecules and x_c that in the critical state, T_c denotes the critical temperature, and $\Sigma\sqrt{m_1}$ the sum of the square roots of the atomic weights of the atoms of a molecule. In a previous paper we have shown that (ϕ) may be taken approximately a function of the temperature only*. The foregoing condition is then expressed by the equation

$$T = \int_{\infty}^{\sigma_3} \frac{(\phi)(\Sigma\sqrt{m_1})^2}{z^5} \cdot dz,$$

where σ_3 denotes the distance of separation of the molecules. Eliminating T from the equation by means of the equation

$$T = H^2\left(\frac{\rho}{m}\right)^{\frac{4}{3}}(\Sigma\sqrt{m_1})^2\dagger,$$

we obtain

$$\sigma_3 = \left(\frac{m}{\rho}\right)^{\frac{1}{3}}\frac{(\phi)\,a}{H^2} = \left(\frac{m}{\rho_c}\right)^{\frac{1}{3}} D,$$

where H^2 and D are the same for all substances at corresponding states, and a is a constant. It follows therefore that the values of σ_3 for gases at corresponding temperatures are the same fraction or multiple of the values at the critical temperatures.

* *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vi. pp. 554, 555; *Phil. Mag.*, May 1910, p. 802.
† *Phil. Mag.*, Oct. 1911, p. 578; May 1910, p. 788; Oct. 1909, p. 509.

Viscosity and Diffusion of Gases.

The results obtained in the previous section indicate that the field of force surrounding a molecule has a great influence on its radius of sphere of action in the gaseous state. To further test this let us assume that a molecule has no appreciable volume but consists of a centre of force possessing a certain mass, and obtain a formula for the coefficient of diffusion on this supposition.

Maxwell has obtained a formula for the coefficient of diffusion of one gas into another on this supposition, assuming that the attraction between two molecules is given by $\frac{B}{z^5}$, where B is a constant which depends on the nature of the gas. This law is the same in form as (3) assuming (ϕ) a constant or a function of the temperature only. The coefficient of diffusion D of a gas 1 into a gas 2 is then given by

$$D = \frac{p_1}{\rho_1 \rho_2} \frac{p_2}{A \left\{ \frac{B}{M_1 M_2 (M_1 + M_2)} \right\}^{\frac{1}{2}}} \frac{1}{p},$$

where p_1 and p_2 denote the partial pressures and ρ_1 and ρ_2 the partial densities of the gases, M_1 and M_2 denote their molecular weights, $p = p_1 + p_2$, and A is a constant. Let us consider the case when the number of molecules 1 is small in comparison with the number of molecules 2, so that $p = p_2$. Since $\frac{p_1}{\rho_1} = \frac{RT}{M_1}$, the equation may then be written

$$D = \frac{RT}{M_1 \rho_2} \frac{1}{A \left\{ \frac{B}{M_1 M_2 (M_1 + M_2)} \right\}^{\frac{1}{2}}} \quad \text{.....(4).}$$

The coefficient of diffusion of a molecule in a gas of the same kind is according to (3) and the foregoing equation given by

$$D = \frac{C_1 T}{(\phi)^{\frac{1}{2}} M_1^{\frac{1}{2}} \Sigma \sqrt{m_1}} \quad \text{.....(5),}$$

where C_1 is a constant. This coefficient of diffusion cannot be measured in practice. But we can transform the equation into a form which is more useful. According to the kinetic theory of gases $D = \frac{\eta}{\rho_1}$, where η denotes the coefficient of viscosity, and equation (5) may be written

$$\eta = \frac{C_2 T M_1^{\frac{1}{2}}}{(\phi)^{\frac{1}{2}} \Sigma \sqrt{m_1}} \quad \text{.....(6),}$$

where C_2 is a constant.

It is most convenient to apply equation (6) to substances at corresponding states since (ϕ) is then constant. Table IV gives

TABLE IV.

	$\eta 10^7$ (Exp.)	$\eta 10^7$ (Cal.)
Carbon tetrachloride	1950	1630
Chloroform.....	1905	1681
Ethyl propionate ...	1074	1006
Benzene...	1057	1194
Methyl formate.....	998	1284
Ethyl oxide	745	969

the values of η for a few substances corresponding to $\frac{3}{5}\frac{4}{5}\frac{9}{6}T_c$, given in a previous paper by the writer*, and the values of η calculated by equation (6) putting $C_2/(\phi)^{\frac{1}{2}} = 10{\cdot}25$. Only a rough agreement between the two sets of values is obtained. But a good agreement cannot be expected, since (ϕ) is strictly a function of the distance of separation of the molecules and of their temperature; moreover, the interaction of the molecules must to some extent be influenced by their actual volume. This point will be reconsidered in a subsequent paper.

In a previous paper the diffusion of one gas into another of a different kind was calculated by means of equation (4). The law of attraction between two molecules which are different is taken in conformity to (3) to be $\frac{K_1 \Sigma\sqrt{m_1}\,\Sigma\sqrt{m_2}}{z^5}$, where K_1 is a function of the temperature. Taking K_1 a constant a fair agreement between calculation and experiment was obtained†.

The Constitution of a Molecule and the Form of (ϕ).

It appears‡ from considerations of the Joule-Thomson effect that the attraction between two molecules separated by a constant distance is roughly inversely proportional to the temperature. Since (ϕ) may be taken approximately a function of the temperature only, it may be written $\frac{k}{T}$, where k is a constant. It will

* *Phil. Mag.*, Sept. 1910, p. 447.
† *Ibid.*, May 1910, p. 807.
‡ *Proc. Camb. Phil. Soc.*, Vol. XVI. Pt vi. p. 557.

TABLE V.

	T	$\eta 10^7$	$\frac{\eta 10^7}{T^{\frac{3}{2}}}$	$\frac{\eta 10^7}{T}$
Argon.....	273	2104	·466	7·70
	372·7	2733	·380	7·33
	456·7	3221	·330	7·05
Helium	273	1891	·419	6·93
	339·6	2348	·374	6·90
	457·6	2699	·275	5·89
Hydrogen, H_2	273	822	·182	3·01
	326·4	976	·166	2·99
	372·2	1059	·148	2·85
	575	1392	·101	2·42
Nitrogen, N_2	251·5	1563	·392	6·22
	293	1840	·367	6·28
	326·5	1894	·321	5·80
Carbon dioxide, CO_2.....	273	1414	·313	5·18
	326·5	1638	·278	5·02
	435·4	2143	·236	4·93
Methyl chloride, CH_3Cl ...	257·7	936	·226	3·63
	372·1	1384	·193	3·72
	455·4	1706	·176	3·74
	575	2139	·155	3·72
Chloroform, $CHCl_3$	273	959	·212	3·51
	290·4	1029	·213	3·62
	334·2	1890	·246	5·66
Ethylene, C_2H_4	273	966	·214	3·54
	326	1096	·186	3·36
	455·4	1530	·158	3·36
	575·6	1826	·132	3·17
Benzene, C_6H_6	273	709	·157	2·60
	373	1176	·163	3·15
Methyl isobutyrate, $C_5H_{10}O_2$	297	754	·147	2·53
	373	1122	·156	3·01
Propyl acetate, $C_5H_{10}O_2$ ...	288	743	·152	2·58
	373	1096	·152	2·94
Isobutyl acetate, $C_6H_{12}O_2$...	289·1	764	·155	2·64
	373	1120	·155	3·00

therefore be of interest to compare the values of η for different temperatures given by equation (6) for two cases: when this expression is put for (ϕ), and when (ϕ) is supposed to be a constant. We should then respectively have $\eta = B_1 T^{\frac{3}{2}}$ and $\eta = B_2 T$, where B_1 and B_2 are constants. The comparison is best carried out by calculating the values of B_1 and B_2 for different temperatures from the facts and comparing them with one another. Table V gives the values of B_1 and B_2 calculated for a number of substances. The interesting result is obtained that the former of the above equations fits the facts best in the case of complex substances, and the latter equation in the case of simple substances. In fact there seems to be a gradual change in the applicability of each equation as we pass from the simplest to the most complex substances or *vice versa*. The results show that the simpler the molecule the less (ϕ) in the law of molecular attraction depends on the temperature. It seems probable from the results that in the case of an atom (ϕ) is very approximately independent of the temperature. The significance of this result will be pointed out towards the end of the paper.

We have obtained evidence in this paper and in previous papers that (ϕ) may as a rough approximation be taken a function of the temperature only. It will be of interest to see whether this fits in with the result that the attraction between two molecules decreases with increase of temperature, for which we obtained evidence in this paper and in previous papers.

The formula for the surface tension then becomes*

$$\lambda = (\phi)(\rho_1 - \rho_2)^2 B,$$

where B is a constant. In a previous paper† we have shown that $\lambda = C(\rho_1 - \rho_2)^4$, where C depends only on the nature of the liquid. Comparing the two equations we see that

$$(\phi) = (\rho_1 - \rho_2)^2 \frac{C}{B},$$

and thus (ϕ) decreases with increase of temperature. It varies approximately inversely as the temperature.

The equation for the internal heat of evaporation becomes‡

$$L = L_1 - L_2 = (\phi)(\rho_1^{\frac{4}{3}} - \rho_2^{\frac{4}{3}})\, D,$$

where D depends only on the nature of the liquid. In a previous paper§ we have shown that (ϕ) (there denoted by A) decreases with increase of temperature in this equation. But the decrease is not so rapid as in the foregoing equation.

* *Phil. Mag.*, Oct. 1911, pp. 566—588. † *Ibid.*, Jan. 1911, pp. 99—101.
‡ *Loc. cit.* § *Phil. Mag.*, May 1910, pp. 795—797.

In the same way we obtain for the intrinsic pressure the equation* $P_n = (\phi)\rho_1^{\frac{7}{3}}E$, where E depends only on the nature of the liquid. Since $P_n = L_1\rho_1$ approximately†, and $L_1 = (\phi)\rho_1^{\frac{4}{3}}D$, we also have $P_n = (\phi)\rho_1^{\frac{7}{3}}D$. We know that in this equation (ϕ) decreases with increase of temperature, and this applies therefore also to the above equation.

The fact that (ϕ) does not vary with the temperature to the same extent in each equation is due to (ϕ) not being strictly a function of the temperature only.

A Formula for the Internal Heat of Evaporation.

In a previous paper we have given a method of calculating the heat of evaporation given the law of molecular attraction and supposing that the internal energy of a molecule is independent of the vicinity of other molecules. The method given can, however, be replaced by one that gives a more accurate result.

The distribution of the molecules must satisfy the conditions given in a previous paper‡. According to these conditions the molecules must be situated at the points of intersection of three systems of parallel equidistant planes.

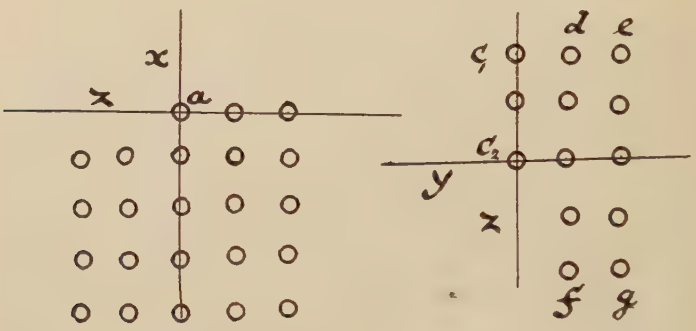
We have shown in a previous paper§ that the internal heat of evaporation per grm. of substance is independent of the mass of substance allowed to evaporate unless it is extremely small. To obtain the correct mathematical expression for the heat of evaporation of a molecule we must suppose, however, that we are dealing with an infinitely large mass of liquid. Let us suppose that it is in the form of a cube, and that the systems of parallel planes by means of which the molecular distribution is defined are taken parallel to the sides of the cube. Suppose a surface layer of molecules moved to infinity, and the molecules of the layer then separated from one another by removing the molecules of each row consecutively beginning at one end of the row, and dealing with the rows consecutively beginning at one edge of the layer. Let the process be repeated till there are no molecules left. The average work done per molecule is the energy necessary per molecule to separate the molecules an infinite distance from one another.

Instead of removing the layers of molecules successively we may suppose them to remain in their position and the molecules of each layer separated in the same way as before. It will be evident now on consideration of the foregoing process that the average work done in removing a molecule of the cube to infinity

* *Phil. Mag.*, Oct. 1910, pp. 666—669.
† *Loc. cit.*, pp. 669, 670.
‡ *Phil. Mag.*, April 1911, p. 537.
§ *Ibid.*, Jan. 1911, p. 90.

is equal to that done in removing the centre molecule of one of the surface layers of the cube, supposing half of the row of molecules in which this molecule lies and all the molecules of the layer on one side of this row to be absent.

Let this molecule be denoted by a in the figure, which gives a horizontal and vertical section through a of the cube. Let the position of the molecule be taken as origin of coordinates and the axes taken parallel to the edges of the cube, and the notation as shown in the figure. Let the distance between two molecules parallel to one of the edges of the cube be denoted by x_a.



Consider the molecule a placed on the axis of x at a distance nx_a from the origin. Its coordinates are now $(nx_a, 0, 0)$. Let the coordinates of a molecule in the cube be (wx_a, ux_a, vx_a), where w, u, and v, it will be noticed, can only assume zero and integral values. The component of attraction of this molecule on the molecule a along the axis of x is therefore, according to the law of molecular attraction (3), equal to

$$\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right) \cdot \left(\frac{nx_a + wx_a}{z}\right) \frac{(\Sigma\sqrt{m_1})^2}{z^5},$$

where z is the distance of separation of the two molecules, and $\left(\frac{nx_a + wx_a}{z}\right)$ the cosine of the angle between the axis x and the line joining the molecules. The value of z from geometrical considerations is given by

$$z = \sqrt{\{(nx_a + wx_a)^2 + u^2x_a^2 + v^2x_a^2\}} = x_a\sqrt{\{(n + w)^2 + u^2 + v^2\}}.$$

The work done in moving the molecule a against the attraction of the remaining molecules of the cube along the axis x from the position $(0, 0, 0)$ to infinity may be divided into three parts. One is the work done against the attraction of the row of molecules

c_1c_2, which consists of half a row of molecules minus one. This is equal to

$$\sum_{v=1}^{v=\infty} \int_0^\infty (\phi) . (\Sigma\sqrt{m_1})^2 \frac{nx_a}{z^6} . dx = \sum_{v=1}^{v=\infty} \int_0^\infty (\phi) . \frac{(\Sigma\sqrt{m_1})^2}{x_a^4} \frac{n . dn}{(n^2+v^2)^3} .$$

Another part is the work done against the attraction of the layer of molecules *d*, *e*, *f*, *g*, which consists of half the surface layer of the cube minus one row. This work is equal to

$$\sum_{v=-\infty}^{v=\infty} \sum_{u=1}^{u=\infty} \int_0^\infty (\phi) . (\Sigma\sqrt{m_1})^2 \frac{(nx_a + ux_a)}{z^6} . dx$$

$$= \sum_{v=-\infty}^{v=\infty} \sum_{u=1}^{u=\infty} \int_0^\infty (\phi) . \frac{(\Sigma\sqrt{m_1})^2}{x_a^4} \frac{(n+u) . dn}{(n^2+u^2+v^2)^3} .$$

The remaining part is the work done against the attraction of the molecules of the cube minus the surface layer. This part is equal to

$$\sum_{v=-\infty}^{v=\infty} \sum_{u=-\infty}^{u=\infty} \sum_{w=1}^{w=\infty} \int_0^\infty (\phi) . \frac{(\Sigma\sqrt{m_1})^2}{x_a^4} \frac{(n+w) . dn}{\{(n+w)^2+u^2+v^2\}^3} .$$

The sum of the foregoing three expressions may be written

$$\phi_1\left(\frac{T}{T_c}, \frac{x_a}{x_c}\right) . \frac{(\Sigma\sqrt{m_1})^2}{x_a^4} .$$

If ρ_1 denote the density of the liquid, ρ_c the critical density, and m_a the absolute molecular weight of a molecule,

$$x_a = \left(\frac{m_a}{\rho_1}\right)^{\frac{1}{3}} \text{ and } x_c = \left(\frac{m_a}{\rho_c}\right)^{\frac{1}{3}} .$$

Therefore if L_1 denote the energy required to separate the molecules of a gram of liquid by an infinite distance from one another

$$L_1 = \phi_1\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_1}\right) . \left(\frac{\rho_1}{m_a}\right)^{\frac{4}{3}} \frac{(\Sigma\sqrt{m_1})^2}{m_a} \quad \ldots\ldots\ldots\ldots(7).$$

Similarly, if L_2 denote the corresponding energy in the case of a gram of the saturated vapour

$$L_2 = \phi_1\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_2}\right) . \left(\frac{\rho_2}{m_a}\right)^{\frac{4}{3}} \frac{(\Sigma\sqrt{m_1})^2}{m_a} \quad \ldots\ldots\ldots\ldots(8),$$

where ρ_2 denotes the density of the vapour. The heat of evaporation L is accordingly given by

$$L = L_1 - L_2 \quad \ldots\ldots\ldots\ldots(9).$$

Deductions supposing (ϕ) *a Function of the Temperature only.*

If we assume that (ϕ) in the law of molecular attraction (3) is a function of the temperature only, we obtain from the previous section that

$$L_1 = 1{\cdot}58\,(\phi)\,\frac{\rho_1^{\frac{4}{3}}}{m_a^{\frac{7}{3}}}\,(\Sigma\sqrt{m_1})^2 \quad \ldots\ldots\ldots\ldots\ldots(10),$$

on evaluating the infinite series. The intrinsic pressure P_n is then given by

$$P_n = \frac{1}{m_a}\left(\frac{dU_1}{dv}\right)_T^* = \left(\frac{dL_1}{dv}\right)_T = -1{\cdot}58\,(\phi)\left(\frac{\rho_1}{m_a}\right)^{\frac{7}{3}}(\Sigma\sqrt{m_1})^2\tfrac{4}{3} = -L_1\rho_1\tfrac{4}{3},$$

where v denotes the volume of a grm. of substance.

On the assumption that matter is evenly distributed in space we obtained $P_n = -L_1\rho_1$ in a previous paper. The values of P_n given by each of these equations agree on the average almost equally well with those given by the equation $P_n = -\frac{T\alpha}{\beta}$†, which depends on the assumption that the internal energy of a molecule is not influenced by the vicinity of other molecules.

We can now test whether the form obtained for L_1 in the previous sections is mathematically correct. It is possible to calculate P_n directly‡. We then have $P_n = -\frac{dL_1}{dv}$§, which is independent of the nature of the law of molecular attraction, where v denotes the volume of a gram of substance. Using the law (3) and assuming that (ϕ) is a function of the temperature only, we obtain

$$2{\cdot}06\,(\phi)\left(\frac{\rho_1}{m_a}\right)^{\frac{7}{3}}(\Sigma\sqrt{m_1})^2 = 2{\cdot}10\,(\phi)\left(\frac{\rho_1}{m_a}\right)^{\frac{7}{3}}(\Sigma\sqrt{m_1})^2,$$

showing that the formula is mathematically correct.

An Absolute Value of (ϕ).

It is of interest to obtain a value for (ϕ) for a given temperature on the supposition that it is a function of the temperature only. Equation (10) may be used for this purpose. In the case of ether at $\frac{2T_c}{3}$ we have $L_1 = 75{\cdot}4 \times 4{\cdot}2 \times 10^7$, $\rho_1 = {\cdot}6907$, $\Sigma\sqrt{m_1} = 27{\cdot}8$,

* *Proc. Camb. Phil. Soc.* Vol. xvi. Pt vi. pp. 543–544.
† *Loc. cit.*
‡ *Phil. Mag.*, Oct. 1910, pp. 666, 667.
§ *Loc. cit.*, p. 543.

$m_a = 74 \times 1{\cdot}61 \times 10^{-24}$ grm., where $1{\cdot}61 \times 10^{-24}$ grm. is the mass of a hydrogen atom as obtained by Rutherford from experiments on the α particle. We obtain accordingly

$$(\phi) = 2{\cdot}97 \times 10^{-45} \text{ (grms.) (cm.) (sec.)}^{-2}.$$

It will be observed that (ϕ) gives approximately the attraction between two hydrogen atoms at $\frac{2T_c}{3}$ separated by unit distance.

The gravitational attraction between two molecules in a liquid separated by the average distance of separation of the molecules, is vanishingly small in comparison with the 'chemical' attraction. For example, the 'chemical' attraction given by $(\phi)\frac{(\Sigma\sqrt{m_1})^2}{z^5}$ between two ether molecules at $\frac{2T_c}{3}$ under those circumstances is equal to $6{\cdot}65 \times 10^{-6}$ dynes. The gravitational attraction is equal to $\frac{km_a^2}{z^2}$, where $k = 6{\cdot}6579 \times 10^{-8}$, that is, equal to $7{\cdot}34 \times 10^{-38}$ dynes. The attraction in the latter case is thus vanishingly small in comparison with what it is in the former.

According to the above value of (ϕ) the 'chemical' attraction is greater than the gravitational for distances of separation of the molecules of the order 10 cm. This shows that the attraction decreases more rapidly with the distance of separation of the molecules for large distances than that given by the inverse fifth power law, as we might expect. But for distances of separation of the order of that of the molecules in the liquid state the approximate expression for the attraction should very approximately represent the facts.

The attraction between two electrical charges e of opposite sign separated from one another by a distance equal to the average distance of separation of the molecules of liquid ether at $\frac{2T_c}{3}$, is equal to $4{\cdot}65 \times 10^{-5}$ dynes. This attraction is greater than that given above for two ether molecules. But the attraction between two molecules much heavier than ether molecules could easily be of the same magnitude.

The Average Velocity of a Molecule in a Substance.

We have shown that the velocity of a molecule in a substance at a point where the forces of the surrounding molecules neutralize one another is the same as in the gaseous state at the same temperature. But at other points the velocity will be much greater due to the attraction of the molecules on one another, and the average velocity is therefore much greater than that corresponding to the temperature. This can be easily proved

to be the case. For example, the increase in kinetic energy of two ether molecules, when they approach one another from the average distance of separation of the molecules in ether at $\frac{2T_c}{3}$ to half that distance, is equal to

$$(\phi).\frac{(\Sigma\sqrt{m_1})^2}{4}\left(\frac{1}{(z/2)^4}-\frac{1}{z^4}\right), \text{ where } z=\left(\frac{m_a}{\rho_1}\right)^{\frac{1}{3}}.$$

Now $\rho_1 = \cdot 6907$, $m_a = 74 \times 1{\cdot}61 \times 10^{-24}$ grm., $(\phi) = 2{\cdot}97 \times 10^{-45}$, $\Sigma\sqrt{m_1} = 27{\cdot}8$, and the increase of kinetic energy is thus equal to $9{\cdot}0 \times 10^{-11}$ ergs, which corresponds to an increase of velocity equal to $6{\cdot}1 \times 10^4 \frac{\text{cm.}}{\text{sec.}}$ for each molecule. The average velocity is probably much greater than this value. It is consequently greater than $3{\cdot}03 \times 10^4 \frac{\text{cm.}}{\text{sec.}}$, the velocity corresponding to the temperature.

It follows therefore that the form of the right-hand side of van der Waals' equation of state, which depends on the assumption that the average velocity of a molecule is independent of the density of the substance, must be considerably modified. This will be carried out in a subsequent paper.

Remarks.

In this and a preceding paper we have endeavoured to separate the effects due to U, the energy necessary per molecule to separate the molecules of a mass of substance by an infinite distance from one another, and u, the internal energy of a molecule. It appears that this is only possible to a certain extent. It appears that U and u always occur together thus $(U + u - u_a)$, where u_a is the value of u of a molecule in the gaseous state. But this will not affect any of the general conclusions we have arrived at in connection with the law of molecular attraction of which U is a function, on the supposition that $(u - u_a)$ may be neglected in comparison with U. It follows directly from the law of corresponding states that U and $(u - u_a)$ are of the same general form, which will be shown in a subsequent paper. It follows also at once from some previous investigations by the writer. The equation for the internal heat of evaporation is

$$L = U_1 - U_2 + u_1 - u_2,$$

where the suffixes 1 and 2 refer to the liquid and its saturated vapour respectively. On deducing an expression for L by means of the law of attraction (3), supposing $(u_1 - u_2)$ negligible in comparison with $(U_1 - U_2)$, we obtain that L must obey the law

of corresponding states*. This is found to agree with the facts. It follows therefore that either the supposition made is true or the general form of $u_1 - u_2$ is the same as that of $U_1 - U_2$, that is, both are of the form

$$\phi_1\left(\frac{T}{T_c}, \frac{\rho_c}{\rho}\right)\left(\frac{\rho}{m}\right)^{\frac{4}{3}}(\Sigma\sqrt{m_1})^2.$$

That the internal energy of a molecule is very likely not changed very much by the vicinity of other molecules follows from the following considerations. In deducing a formula for the energy necessary to separate the molecules of a substance by an infinite distance from one another we may suppose the molecules devoid of motion and distributed in space in a certain way. One of the conditions determining this distribution is that the force on each molecule by the surrounding molecules must be zero. It follows therefore that if the molecules consist of points they would be, whatever the density of the substance, in the same condition at their mean positions as in the gaseous state, and would therefore probably possess the same internal energy in all cases. But since it is fairly certain that the atoms of a molecule are not concentrated at a point, the internal energy must be influenced by the surrounding molecules. Thus when a molecule is at its mean position the effect of the surrounding molecules is to produce a radial force acting outwards from a point in the molecule, which neutralizes the attraction between the atoms to a certain extent. This would change the configuration of the molecule and consequently its internal energy. But one would expect that this change in internal energy would not be large.

A change in the configuration of the atoms in two molecules would produce a change in their law of attraction. Thus if the distances of separation of the atoms of each molecule in a substance are increased, i.e. each molecule is expanded, the attraction of the molecules upon one another is increased if the number of molecules per c.c. remains unchanged. This will at once be evident when it is pointed out that for any two molecules the distance between the atoms nearest to one another is decreased while the distance between the atoms furthest away from one another is increased. The increase in the attraction between the atoms in the former case is greater than the decrease of attraction in the latter case, and thus on the whole there is an increase in attraction between the molecules. Thus the law of attraction between two molecules should depend to some extent on the vicinity of other molecules.

* *Phil. Mag.*, Oct. 1911, p. 577.

The internal energy of a molecule is known to increase with increase of temperature. The increase is the greater the more complex the molecule. When a molecule consists of a single atom there appears to occur no change in internal energy. This suggests that the change in internal energy of a molecule with change of temperature is due to a change of the configuration of its atoms. We should therefore expect from the foregoing considerations that there would also occur a change in the attraction between two molecules with change of temperature, and that this change would be the greater the more complex the molecule. This fits in with the results obtained in the second section of this paper, according to which (ϕ) depends less on the temperature for simple molecules than for complex.

It follows also that the further two molecules are apart, that is, the greater their distance of separation is in comparison with their dimensions, the less will the attraction be affected by the temperature. This fits in with a deduction made in a previous paper*.

It is difficult to obtain exact information about the relative values of U and $(u - u_a)$. But there is indirect evidence that $(u - u_a)$ is of a smaller order of magnitude than U.

Thus on the assumption that matter is evenly distributed in space and that $u - u_a = 0$ we obtained that $P_n = -L_1\rho_1$. This equation would also approximately hold if the energy expended per molecule in removing a layer of molecules from the surface of a liquid is large in comparison with the energy expended per molecule in separating the molecules of the layer after its removal. We also obtained the formula $P_n = -\frac{T\alpha}{\beta}$, on the assumption that $\left(\frac{du}{dv}\right)_T$ is negligible in comparison with $\left(\frac{dU}{dv}\right)_T$. The values of P_n given by these two equations agree roughly with one another, showing that the assumptions underlying them are at least approximately true.

If we neglect $(u - u_a)$ in comparison with U, and $\left(\frac{du}{dv}\right)_T$ in comparison with $\left(\frac{dU}{dv}\right)_T$, or put $\frac{du}{dT} = \frac{du_a}{dT}$, $\left(\frac{dU}{dT}\right)_v$ is found to be always negative. Now it is unlikely that this would be the case if $(u - u_a)$ were of the same order of magnitude as U. The results obtained in this paper are evidence that $\left(\frac{dU}{dT}\right)_v$ should be negative.

Further evidence that $(u - u_a)$ is of a smaller magnitude than

* *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vi. pp. 553, 554.

U, and that the same applies to the differential coefficients, will be brought forward in subsequent papers.

From the foregoing considerations in this section it appears that a change in the internal energy of a molecule is associated with a change in the configuration of the atoms, which are probably not concentrated at a point, and that this change in configuration must be attended by a change in the law of molecular attraction. The force of attraction exerted by a molecule in different directions cannot be the same if the atoms are not concentrated at a point. The law of attraction deduced from the surface tension and the internal heat of evaporation of liquids is a mean law since the molecules are probably undergoing motion of rotation as well as of translation in a liquid. This mean law must depend on the configuration of the atoms in the molecules as well as on their number and their nature, and therefore differs considerably from that expressing the attraction between two atoms. Thus it is conceivable that the law of molecular attraction may involve the critical constants, and contain the temperature as one of the variables.

If two molecules are not undergoing rotation the attraction upon one another would be expressed by the sum of a number of terms each of which expresses the attraction of an atom in one of the molecules on an atom in the other molecule. Each term consists of the product of the attraction constants of two atoms, multiplied by a function of their distance of separation. Since the distance of separation is different in each case, the values of these functions differ from one another. Therefore if the attraction between two molecules is expressed as the product of the sum of the attraction constants of the atoms of one of the molecules into the sum of the attraction constants of the other molecule, multiplied by a function of their distance of separation, this can only approximately represent the facts, for it amounts to assuming that the atoms of each molecule are concentrated at a point. The general form of the law of molecular attraction including all the deviations from the law (3) has already been given in a previous paper*.

* *Phil. Mag.*, Oct. 1911, pp. 578—580.

A simple viscometer for very viscous liquids. By G. F. C. Searle, Sc.D., F.R.S., University Lecturer in Experimental Physics, Fellow of Peterhouse.

[*Read* 20 May 1912.]

§ 1. *Introduction.* The viscosity of treacle is so great that it cannot be measured conveniently by allowing the liquid to flow through a tube of small bore, as is done in the case of water, for at 12° C. the viscosity of treacle is about 400 C.G.S. units, and that of Lyle's "golden syrup" is about 1400, while that of water is only 0·0146. But the great viscosity of treacle allows the use of another method, in which the mechanical actions called into play are more conspicuous than when a liquid flows through a tube. The method described below was introduced into my class at the Cavendish Laboratory in November 1911 and has been found to be interesting and instructive to the students and to be satisfactory to the demonstrators.

The method, which is well known in principle, is to cause a vertical cylinder to rotate within a coaxal vertical cylinder containing liquid and to determine the angular velocity of the inner cylinder for a known value of the driving couple.

In the elementary theory, the motion of the liquid between the vertical sides of the cylinders is assumed to be the same as if the cylinders were infinite in length. In practice, one end, at least, of the rotating cylinder is exposed to viscous action and thus a correction for that end becomes necessary. In the original apparatus constructed in the Cavendish Laboratory no arrangement was made for determining this correction, but in the case of the apparatus shown in Fig. 2 this correction can be readily found. I am much indebted to Mr W. G. Pye for his assistance in designing the improved apparatus.

§ 2. *Elementary theory.* Let the viscosity of the liquid between the cylinders be μ dynes per square cm. per unit rate of shearing (i.e. one radian per second). Let the inner cylinder of radius b cm. be made to rotate about its axis with the uniform velocity Ω radians per second by a couple, the internal radius of the outer (fixed) cylinder being a cm. Let the angular velocity of the liquid at a distance r cm. from the axis be ω radians per second, and at the distance $r+dr$ let it be $\omega+d\omega$. Since it is only the motion of the liquid at $r+dr$ *relative* to that at r which

we have to consider, we may impart a negative angular velocity ω to the whole system without affecting the stresses due to viscosity. Then the particles at distance r from the axis are at rest and those at $r+dr$ move with velocity $d\omega\,(r+dr)$, since the angular velocity which they *now* have is $d\omega$. To the *first* order the velocity is $r\,d\omega$. The tangential stress at the surface of a (geometrical) cylinder of radius r is therefore

$$\mu r \frac{d\omega}{dr} \text{ dynes per square cm.}$$

This stress tends to make the liquid within the cylinder of radius r rotate in the opposite direction to the inner metal cylinder since $d\omega/dr$ is negative.

Let the couple required to maintain a length h cm. of the inner cylinder in angular velocity Ω be G dyne-cm. Since there is no angular *acceleration* of the liquid, the couple exerted by viscous action upon the liquid within a cylinder of radius r and length h is also G. This couple is obtained by multiplying the viscous stress by the area $(2\pi rh)$ of the curved surface of the cylinder of radius r and also by the radius r. Hence

$$G = -2\pi rh \,.\, \mu r \frac{d\omega}{dr} \,.\, r = -2\pi \mu h r^3 \frac{d\omega}{dr}, \quad \ldots\ldots\ldots(1)$$

or

$$\frac{d\omega}{dr} = -\frac{G}{2\pi \mu h} \cdot \frac{1}{r^3}. \quad \ldots\ldots\ldots(2)$$

The solution of this differential equation is

$$\omega = \frac{G}{2\pi \mu h} \cdot \frac{1}{2r^2} + C,$$

where C is a constant such that $\omega = 0$, when $r = a$. Hence

$$\omega = \frac{G}{4\pi \mu h}\left(\frac{1}{r^2} - \frac{1}{a^2}\right). \quad \ldots\ldots\ldots(3)$$

When $r = b$, the angular velocity is Ω, and thus

$$\Omega = \frac{G}{4\pi \mu h}\left(\frac{1}{b^2} - \frac{1}{a^2}\right). \quad \ldots\ldots\ldots(4)$$

Hence we find for the viscosity

$$\mu = \frac{G(a^2 - b^2)}{4\pi \Omega h a^2 b^2}. \quad \ldots\ldots\ldots(5)$$

In practice, the couple G is produced by the weights of two loads each of M grammes acting on a drum of effective diameter D cm. Hence $G = MDg$. The angular velocity is found from T

seconds, the time of one revolution of the cylinder, and thus $\Omega = 2\pi/T$. The formula thus becomes

$$\mu = \frac{gD(a+b)(a-b)}{8\pi^2 a^2 b^2}\left(\frac{MT}{h}\right). \quad \ldots\ldots\ldots\ldots\ldots(6)$$

The method of obtaining the correction due to the finite length of the inner cylinder will be best explained after the description of the viscometer.

§ 3. *The viscometer.* The instrument is shown diagrammatically in Fig. 1. The inner cylinder turns on pivots in

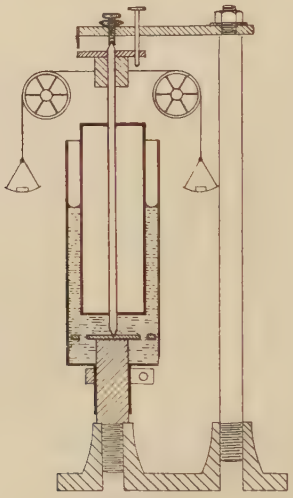


Fig. 1.

bearings at top and bottom. The lower bearing is at the top of a cylindrical pillar rising from the base of the instrument, and the upper bearing is on an arm carried by a vertical rod. The axle supporting the inner cylinder also carries a drum, and the cylinder is caused to rotate by means of two masses supported by a thread wound round the drum and passing over two ball-bearing pulleys. The outer cylinder is clamped to the pillar by a clamp acting on a partially split tube which makes a treacle-tight joint with the pillar. The top of the pillar carries a perforated baffle plate, loosely fitting the outer cylinder. The treacle or other liquid fills the space between the baffle plate and the bottom of the fixed cylinder and also part of the space between the two cylinders, as indicated in Fig. 1. It will be seen that the length of the inner cylinder which is immersed in the liquid will increase if the outer cylinder be made to move upwards on the pillar.

The baffle plate prevents the rotation of the inner cylinder from causing any appreciable motion of the liquid in the space below the baffle plate.

The details of the apparatus are better seen in Fig. 2. A slot about 3 mm. wide is cut in the side of the fixed cylinder and is covered by a plate of glass cemented to the cylinder and secured by a brass plate. The inner cylinder has a scale of millimetres engraved upon it, and, by looking through the glass plate, the length of the inner cylinder which is immersed in the liquid can be read off. Above the drum, the axle carries a disk with a mark on its edge, by aid of which the revolutions of the cylinder are counted. In the most recent form, a locking pin, passing through the arm at the top of the instrument, as indicated in Fig. 1, enables the inner cylinder to be held fixed.

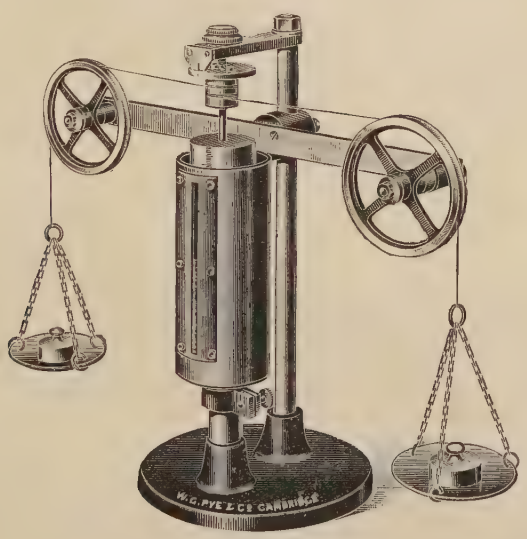


Fig. 2.

§ 4. *Experimental method.* The outer cylinder is first clamped on the pillar in such a position that only a small length—a centimetre or so—of the inner cylinder is immersed in the liquid. If the level of the liquid has been *lowered* it will be necessary to wait for a few minutes to allow the viscous liquid to drain off the sides of the cylinders. After the reading of the liquid on the scale engraved on the inner cylinder has been taken, that cylinder is turned round so as to wind the threads on to the drum. The cylinder is then secured by the locking pin until the observer is ready to determine the time occupied by some convenient number

of revolutions. Equal masses are placed in the two pans; it is convenient to previously adjust each pan to some definite mass—say 10 grms. The time of a number of revolutions is then determined and the time, T secs., for one revolution is deduced. If the corresponding total load hung from each thread be M grms., it will be found, on repeating the observation with various loads, that MT is constant for a given level of liquid. This result confirms the fundamental assumption that the viscous stress at each point is proportional to the rate of shearing of the liquid.

The outer cylinder is then clamped a little higher up on the pillar so as to raise the level of the liquid by about a centimetre and the value of MT is again determined. This process is repeated with approximately equal steps in the level of the liquid as often as the construction of the instrument allows. The reading of the liquid on the inner cylinder is recorded at each stage.

The values of MT are then plotted, as in Fig. 3, against l, the length of the inner cylinder (measured from its lower end) immersed in the liquid. (The diagram represents the observations

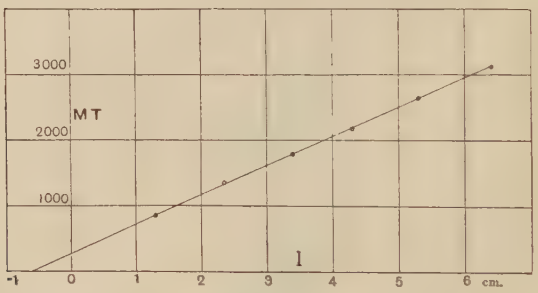


Fig. 3.

recorded in Table I below.) It will be found that the points lie on a straight line, which cuts the axis of l at a distance from the origin on the negative side corresponding to a length k of something like half a centimetre. Hence, the couple required to rotate the inner cylinder at a given angular velocity is proportional to $l+k$, and thus k is the end-correction for the inner cylinder. As will be seen in Table I, the arithmetical values of $MT/(l+k)$ will be found to be very nearly constant.

The other measurements are easily taken. The diameter of the inner cylinder is found by calipers. The radius of the outer cylinder is determined by finding the mass of water which fills it. For this purpose the pillar is unscrewed from the base and is then drawn out of the outer cylinder; the hole at the bottom of the cylinder is plugged with a rubber stopper, the upper end being made flush with the floor of the cylinder. The *effective*

diameter of the drum is found by adding the diameter of the thread to that of the drum itself.

Since the viscosity of treacle diminishes *very rapidly** as the temperature rises, care must be taken to keep the temperature of the apparatus as nearly constant as possible during the series of observations. When, however, the correction for the lower end of the inner cylinder has been found, a single observation is sufficient to determine the viscosity at any particular temperature. The apparatus has been made compact so that it can be placed in a water bath for the purpose of bringing it to any desired temperature.

§ 5. *Practical example.* The following record gives details illustrating the determination of the viscosity of Lyle's golden syrup by the viscometer. The temperature throughout was 12·3° C.

Radius of outer cylinder, found by mass of water contained $= a = 2{\cdot}543$ cm.
Radius of inner cylinder ... ... $= b = 1{\cdot}865$ cm.
Effective diameter of drum ... ... $= D = 1{\cdot}88 + 0{\cdot}03 = 1{\cdot}91$ cm.
Mass of each pan ... ... $= 10$ grms.

To determine the correction for the lower end of the inner cylinder, the observations in Table I were made. The time for three complete revolutions was observed in each case.

Table I.

Load M grm.	Time for one rev. T secs.	MT grm. sec.	Length in liquid l cm.	$l+k$ cm.	$\frac{MT}{l+k}$ grm. sec. cm.$^{-1}$
30	27·9	837	1·30	1·85	452
40	33·3	1332	2·35	2·90	459
60	29·9	1794	3·40	3·95	454
80	27·3	2184	4·30	4·85	450
90	29·5	2655	5·30	5·85	454
100	31·2	3120	6·40	6·95	449

When MT was plotted against l, as in Fig. 3, the resulting straight line indicated that k, the correction for the end, was 0·55 cm. Using this value of k, the last column in Table I has been calculated to show how nearly $MT/(l+k)$ approaches constancy. The mean value of $MT/(l+k)$ from Table I is

453 grm. sec. cm^{-1}.

* At 7° C. the viscosity is more than double that at 14° C.

To test the constancy of MT for a given depth of liquid, the observations in Table II were made with

$$l = 6{\cdot}40 \text{ cm. or } l + k = 6{\cdot}95 \text{ cm.}$$

TABLE II.

Load M grammes	Time for one rev. T seconds	MT grm. sec.
60	52·7	3162
80	39·2	3136
100	31·2	3120
120	26·0	3120
140	22·3	3122

The mean value of MT from Table II is 3132 grm. sec., agreeing closely with the mean value given by Table I. Hence $MT/(l+k) = 3132/6{\cdot}95 = 450{\cdot}7$ grm. sec. cm^{-1}. Putting $l+k$ for h in (6), we find

$$\mu = \frac{gD(a+b)(a-b)}{8\pi^2 a^2 b^2}\left(\frac{MT}{l+k}\right)$$

$$= \frac{981 \times 1{\cdot}91 \times 4{\cdot}408 \times 0{\cdot}678}{8\pi^2 \times 6{\cdot}467 \times 3{\cdot}478}(450{\cdot}7)$$

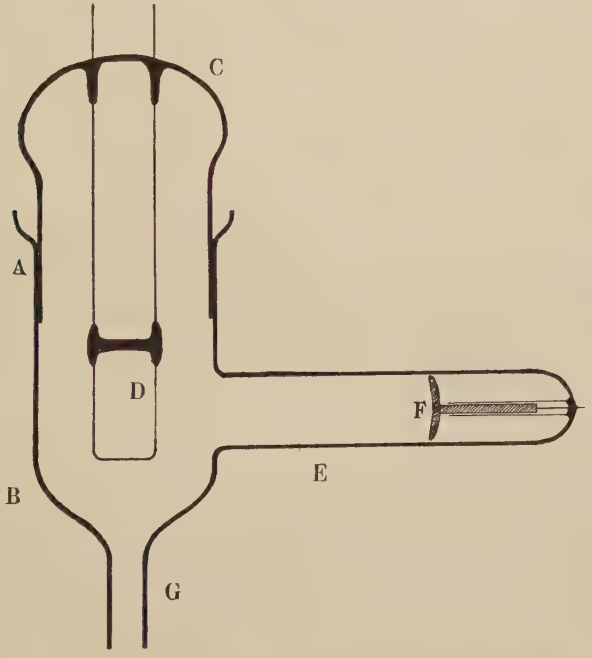
$$= 1421 \text{ dynes per square cm. per unit rate of shearing.}$$

At the same temperature of 12·3° C., the viscosity of black treacle is about 400, and that of water is about 0·0146 C.G.S. units.

Note on the Spectrum of Argon. By G. Stead, B.A., Clare College.

[*Read* 20 May 1912.]

As is well known, two distinct spectra are produced by argon, called respectively the red and blue spectra. The former is obtained by analysis of the light from the capillary portion of an ordinary spectrum tube when a discharge from an induction coil is sent through it. If now a suitable capacity be inserted in the circuit the capillary changes in colour from rose to bright blue. The blue spectrum can also be obtained without a capacity pro-



vided that a large coil and a narrow capillary are used. When the capillary portion of a tube is giving the red spectrum the glow round the cathode is bluish in colour and is found to show a mixture of the two spectra. It would seem therefore that, broadly speaking, the blue spectrum is to be regarded as a high intensity spectrum and the red as a low intensity spectrum. But this is, of course, very general. It is not known whether the determining

factor is average current density, maximum current density, potential gradient, temperature, or some other cause. It occurred to me that it might be worth while to study the spectra of argon by means of a tube provided with a lime cathode. The advantages of the method are:

(i) the ease with which the current, voltage and temperature of the strip can be varied.

(ii) the ease with which the comparatively large currents obtained by the use of a lime cathode can be measured.

It was hoped that by a change of one or more of the variables the red and blue spectra might be obtained at will.

After trying several types of discharge tube the final form adopted was that shown in the accompanying figure. The tubes *AB* and *C* were about 2·5 cm. in diameter and were joined at *A* by means of a ground glass joint and mercury seal. The latter enabled the joint to be made air-tight without the use of grease. Through *C* were sealed two stout platinum wires carrying a thin platinum strip *D* which formed the cathode. The current required to raise *D* to a white heat was about 5 ampères. A short side tube *E*, about 1 cm. in diameter and 5 cm. long, contained an aluminium anode *F*, placed on the same level as the cathode *D*. The beam from the cathode passed down this tube. *G* was a tube connecting the apparatus to the pump, supply of argon, etc.

The argon used was obtained from Hilger's, and to make sure that all nitrogen was removed, it was purified by the usual process of sparking for many hours with oxygen. The high potential required to work the tube was obtained by means of a battery of small storage cells. Various voltages were tried ranging from 100 to 2000. Experiments were made with pressures from about half a millimetre to the lowest pressures conveniently obtainable by the aid of charcoal and liquid air. For the examination of the spectra a Hilger constant deviation wave-length spectroscope was employed.

Results. So long as the pressure was not lower than about ·02 mm. a definite and fairly bright positive column was produced. This always showed the red spectrum without a trace of the blue spectrum. At lower pressures the positive column practically ceased to exist. The beam from the cathode was always blue in colour, and was usually very bright except when the voltage used was low. With the strip as hot as possible, and a voltage of about 2000 it was found that the spectrum of the cathode beam was practically identical with that of the light from an ordinary vacuum tube through which a Leyden jar discharge is passed, i.e. almost pure blue. If the temperature and voltage were reduced the red spectrum began to appear, but was always a good deal less bright than the blue. When the beam was very faint owing to low

voltage, or was on the point of disappearing owing to the low temperature of the strip, the spectrum presented much the same appearance (except as regards intensity) as the spectrum of the negative glow in an ordinary discharge. Thus at the anode only the red spectrum could be produced, whilst at the cathode a mixture of red and blue or pure blue alone could be obtained according to circumstances.

As previously remarked, the positive column was absent at low pressures. It was found, however, that by applying a magnetic field, so as to deflect the beam from the cathode upwards and prevent it from entering the anode tube *E*, a positive column could be produced at pressures when, in ordinary circumstances, no trace of one would be visible. The positive column, however, still showed the same spectrum, viz. pure red.

Thus the main object of the experiment—to obtain the red or blue spectrum in the same part of the tube by simply altering the conditions—failed. The chief interest of the work lies therefore in the fact that at the cathode either a mixture of red and blue (corresponding to the ordinary negative glow spectrum) or pure blue (corresponding to the Leyden jar spectrum) could be obtained at will by altering either the temperature of the strip or the voltage applied to the tube.

In conclusion, I wish to express my best thanks to Professor Sir J. J. Thomson for his interest in the work.

Stachypteris Hallei: *a new Jurassic Fern.*

By H. Hamshaw Thomas, M.A., Downing College, Curator of the Botanical Museum, Cambridge.

[*Read* 20 May 1912.]

(Plate IV.)

In 1847 Pomel* described some small ferns from the Oolitic rocks of Verdun and Châteauroux which apparently bore small fertile segments situated at the extremities of some of the pinnae; he instituted the generic name of *Stachypteris* for these specimens. They were first figured and redescribed by Saporta†, who defined the genus as follows:

Frons bi-tripinnata parvula segmentis inferioribus saepe ceteris productioribus, pinnae ultimae pinnatifidae partitaeque, pinnulae coriaceae minutae basi adnatae vel plus minusque restrictae confluentes aut distinctae enerviae vel uninerviae, nervulis caeterum, si adsint, immersis; fructificatio constans e pinnulis contractis inter se coalitis supra convexo-bullatis subtus concavis marginibusque revolutis sporangia intus inclusa foventibus spicas elongatis squamis distiche ordinatis conflatas mentiens, summis pinnarum pinnularumque rachis inserta.

Pomel had considered that the fertile spikes were formed of more or less separate imbricating scales and compared them with the fertile segments of *Lygodium*. Saporta, however, did not accept this view. He considered them to have been formed of prolongations of a pinna with reduced contiguous pinnules borne on both sides and united together, the boundaries of the pinnules being marked by furrows and their margins being recurved to form the indusium. As will be pointed out later, it seems probable that Pomel's original view is the more correct. Apparently nothing could be made out from these specimens as to the form of sporangia and spores.

Pomel distinguished two species *S. spicans* and *S. litophylla* separated by the form of the segments and by the position of the fertile spikes. Saporta added a third species *S. minuta* with more finely divided segments. Saporta‡ subsequently figured some sterile specimens of *minuta* and *litophylla* from the Jurassic of Portugal; in the absence of fertile fronds, however, it is impossible to be certain of the correctness of these determinations. Somewhat similar fronds, but without any clear evidence of fertile segments,

* *Amt. Ber. Versam. Gesells. deutsch. Naturforsch. Aachen*, 1847, p. 337.

† *Paléontologie Française*, Ser. II. "Plantes Jurassiques," 1873, Vol. I. p. 379, Pl. 49, figs. 2—6, Pl. 50, figs. 1—5, Pl. 51, fig. 1.

‡ *Flore Foss. Portugal*, 1894, p. 48, Pl. IV. figs. 1, 10, VI. 14, VII. 4, VIII. 5 *a*, X. 15.

have been described by Salfeld* from the Coralline Oolite of North Germany as *S. litophylla.* Here again we cannot be sure that we have a true *Stachypteris.* No localities other than the above appear to have yielded examples of these rare ferns.

In 1910 an interesting discovery was made near Whitby, Yorkshire, by Dr T. G. Halle, of a small specimen which was referable to this genus. It showed parts of fronds rather imperfectly preserved in a micaceous shale but with some very interesting features (cf. Pl. IV, figs. 2, 3). This specimen is preserved in the Royal Museum at Stockholm, and I am indebted to Prof. Nathorst and Dr Halle for kindly placing it at my disposal for examination. In April 1912 I was fortunate enough to find two further specimens of the same type in the bed of grey shale in the Marske quarry near Saltburn. This bed belongs to the lower part of the Lower Estuarine Series, it is of the same age as the plant beds at Whitby and Hayburn Wyke, but rather older than those of Scarborough and Gristhorpe. From the materials now available it is possible to provide further information as to the structure of the ferns of this group.

The Marske and Whitby specimens show some differences in form which may be perhaps attributed to the more mature condition of the latter at the time of fossilisation, the differences are, however, not great, and I consider that they both belonged to the same species, which I have named after my friend Dr Halle.

The species may be described as follows: Fronds tri or quadripinnate probably somewhat deltoid in outline. Axis of the frond slender. Pinnae of the second order divided into five or six pinnules and sometimes terminated with a fertile spike. Pinnules rounded or deltoid in form sometimes slightly notched. Veins slender, inconspicuous, simple or branched. The fertile secondary pinnae have a distal linear prolongation bearing two or more rows of small deltoid segments each of which appears to bear a single sporangium, the margins of the segments were probably modified to form an overlapping indusium. The sporangia when mature formed a dense spike-like group, each possessed a well-marked vertical or slightly oblique annulus. The spores were large, somewhat tetrahedral in shape with a tetrad scar and thickened walls. The thickenings on the walls form a very prominent reticulum.

The Marske specimen (Pl. IV, fig. 1) appears at first sight to have a central rather stout rachis from which the pinnae spring, the stem shown in the figure is, however, not the true axis of the frond whose lamina is seen, but is a structure lying parallel to and above the frond axis. The latter has a breadth of about half a millimetre, it lies almost touching the larger stem and suggests

* *Kenntniss jura. Pflanzereste Norddeutschland, Palaeontographica*, 1909, Bd. LVI. p. 11, Taf. III. fig. 4, Taf. IV. fig. 6.

a possible connection with the latter. It seems not unlikely that we are here dealing with only a small portion of a large and highly divided frond.

The general form of the lamina can be made out from the figures, the small ultimate segments or pinnules are for the most part somewhat ovate in shape with bluntly pointed apices. Sometimes they are rather cuniform or slightly notched, they are usually quite distinct but are sometimes confluent. The veins are not conspicuous, each segment is traversed by a fine vein which, in the larger segments, gives off branches of the sphenopteroid type. In close association with the fertile specimen from Whitby we have a finely divided portion of a frond, shown in figs. 3, 3 *a*. Some of its pinnules are like those of the Marske frond, but in others the ultimate segments are more divided (fig. 3 *a*). Several sterile fronds have been found at Marske, none of which can be confidently assigned to *Stachypteris*, some of them have narrower ultimate segments more deeply divided and are perhaps identical with *Coniopteris quinqueloba* (Phil.), others are similar in form to the fertile specimen but have slightly larger segments. As before observed, it is practically impossible to identify these sterile fronds with any certainty owing to the extreme variability which some of these forms appear to exhibit.

The fertile spikes are seen at the apices of the secondary pinnae, the material does not show whether they were borne also at the apices of the primary pinnae (as was the case in some of Pomel's specimens). In the Whitby examples the fertile pinnae possess only two or three sterile pinnules below the fertile portion, but in one of the Marske fronds there may be as many as five or six pinnules. The exact structure of the spike is still somewhat uncertain, it is composed of small segments given off from the axis (see fig. 1 *a*) but owing to compression it is difficult to make out whether they were arranged in an imbricating manner, or whether they were small inrolled segments fused together.

There are, however, several indications that the spikes were of the type seen in *Lygodium*. It would appear that each segment bore a single sporangium. In one case part of a sporangium is seen projecting from under the overlapping segment (or indusium) and the sporangia were almost as large as the segments. In the Whitby specimen no segments or indusia can be made out, the fertile spike (see figs. 2 *a* and 4) appears to consist of three rows of sporangia borne in a very regular fashion, and at first sight it might appear that this belonged to a fern distinct from the Marske form, but the discovery of the same characteristic spores in both showed that this was not the case. It appears as though the upper portions of the indusia or fertile segments withered and became inconspicuous on the ripening of the sporangia. Though only two rows

of sporangium bearing segments appear to be present in the Marske forms it is possible that a third row might have been present on the opposite side to that shown in the figure.

The sporangia had a diameter of about half a millimetre, they had a very distinct annulus which was either vertical or slightly oblique (see fig. 4), probably the latter. In any case it was not of the apical type seen in the modern members of the Schizaeaceae. The sporangia contained a number of large spores which may be seen by treating portions of the spike for some time with Schultz's solution (HNO_3 and $KClO_3$). Most of the spores are somewhat tetrahedral in shape, but others are more rounded, they had a diameter of about ·045—·06 mm., the tetrad scar can occasionally be seen.

The walls of the spores were much thickened in a very characteristic reticulate manner, as shown in the photograph (fig. 5). The spaces in the meshes were sunken and the edges of the spores often appear in consequence to bear a series of prominent papillae. This form of thickening has not yet been noticed on the spore walls of any other Jurassic fern and it may perhaps serve as a ready means of identifying this type.

The foregoing observations on the structure of the sporangia and fertile spikes suggest that the genus *Stachypteris* does not possess any close affinities with the modern groups of ferns. Pomel originally compared it with the Schizaeaceous form *Lygodium* but Saporta considered that it was most closely allied to the genus *Cheilanthes*, basing his belief on the view of the structure of the fertile spike referred to above. The discovery of the sporangia apparently borne singly on each segment shows that the latter view cannot be retained. For the same reason *Lygodium* would appear to be perhaps the most nearly related modern genus so far at least as regards the apparently monangic nature of the sorus. The spores of the Schizaeaceae can also be compared with those of the present form in their strongly thickened walls. But on the other hand one of the most characteristic features of the Schizaeaceae is the small apical annulus, while in the present genus the annulus if not vertical is only slightly oblique and probably approaches that of the Cyatheaceae in this respect. *Stachypteris* may then be regarded as exhibiting some features in common with both the Schizaeaceae and Cyatheaceae. It does not seem to be closely allied to the Hymenophyllaceae though at first sight the spike of sporangia in the Whitby specimen might suggest this affinity.

The Cyatheaceae were present in some abundance in the Jurassic flora while the Schizaeaceae were represented by *Klukia* with its sporangia terminated with an apical annulus, and probably

by other forms. Berry* has described a fern from the Lower Cretaceous rocks of Maryland, *Schizaeopsis expansa*, which bears small fertile spikes at the margins of its fronds; nothing has been made out as to the structure of the sporangia in this form and therefore it may be considered as a possible relation of *Stachypteris* until the contrary is proved. Of course in this case the difference in the vegetative structure of the fronds is very great.

While, therefore, I regard *Stachypteris* as belonging to a group of ferns intermediate in their characters between the Cyatheaceae and the Schizaeaceae, it is to be hoped that further work will throw more light on its affinities or on the possible existence of such an intermediate group.

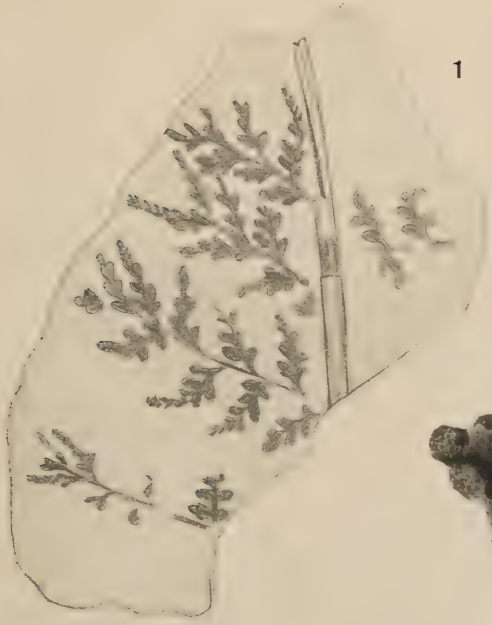
In conclusion I must express my thanks to Prof. Seward, to Prof. Nathorst and to Dr Halle for their kind interest and help in this work.

* *Annals of Botany*, 1911, p. 193, Pl. XII.

Explanation of Figures on Plate IV.

Figures by Frau Ekblom and the author.

Fig. 1. Fertile frond from Marske × $\frac{3}{2}$. Fig. 1 *a*. Part of fertile pinna from the same × 15. Fig. 2. Fertile pinna from near Whitby, nat. size. Fig. 2 *a*. Ditto × 3. Fig. 3. Part of sterile frond from Whitby specimen, nat. size. Fig. 3 *a*. A pinna of the same × 3. Fig. 4. Fertile spike of specimen shown in 2, enlarged to show sporangia (somewhat diagrammatic) × 12. Fig. 5. Spores from same specimen showing reticulate markings × 140.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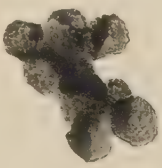
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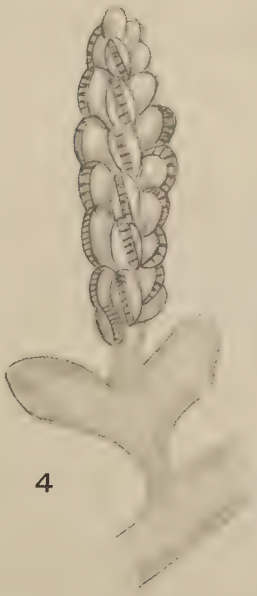
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3a

Some Observations on Electrograms of the Frog's Heart. (Preliminary note.) By George Ralph Mines, M.A., Fellow of Sidney Sussex College. (From the Physiological Laboratory, Cambridge.)

[*Read* 20 May 1912.]

(Plates V—IX.)

The records which form the subject of this note were made during the course of an enquiry, still in progress, the main interest of which lies in the analysis of the action of electrolytes on heart muscle*. I have thought it worth while to give some separate account of certain observations made incidentally which may be of interest in connexion with the interpretation of the electrocardiogram†.

The experiments were made on the exposed hearts of frogs. The electrical changes were registered with the aid of Einthoven's string galvanometer (Camb. Sci. Inst. Co.'s model). The non-polarisable electrodes were of a type described elsewhere‡: they were connected by threads saturated with Ringer's solution to two regions of the heart, one of these being the apex of the ventricle, the other the base of the ventricle or the region of the sinus venosus. The potential differences available in direct derivation from the heart are considerable and thus a high tension of string can be used in the galvanometer, ensuring records which give a true picture of the time relations and extent of the potential changes. In the original curves (from which the figures are reduced) a deflection of about 4 millimetres was produced by a P.D. of 1 centivolt. Simultaneous records of the movements of auricles and ventricle were taken on the sensitive paper by projecting the shadows of light levers on to the illuminated slit, the levers being connected by fine silk threads, one to the tip of the ventricle, another to an auricle. In some of the experiments in which the heart was perfused with fluid by means of a cannula tied in the inferior vena cava, the systolic output was also recorded by connecting a rubber tube to a cannula placed in one of the aortae (the other being tied) and allowing the drops

* The expenses of this research are defrayed in part by grants from the Government Grant Committee of the Royal Society.

† Samojloff (*Pflüger's Archiv*, 135, p. 417, 1910) suggests that the expression "Electrocardiogram" should be reserved for records taken by indirect derivation, as in clinical work, just as "Cardiogram" is commonly used for the mechanical record taken from the chest wall. The electrical record taken by direct derivation is called an Electrogram, that from the ventricle alone Ventricle Electrogram and so forth.

‡ Mines, *Kolloidchemische Beihefte*, III, p. 196, 1912.

pumped out to fall in front of the slit. An example of a tracing taken in this way is shown in fig. 1. In this, as in the other figures, the time is marked in seconds with a Jacquet clock. Samojloff has called attention to the remarkable similarity which exists between the normal human electrocardiogram and the electrogram obtained by direct derivation from the base and apex of the frog's heart. Fig. 2 shows a typical instance of the latter. Using the nomenclature of Einthoven, the P, R and T waves are very clearly seen. The P wave precedes the auricular systole, the R wave precedes the ventricular systole and is the most constant feature of the electrogram, the T wave occurs during or at the close of the ventricular systole. Fig. 3 shows an electrogram obtained by derivation from the base and apex of the ventricle. It will be noted that there is no P wave. There seems to be no doubt that the R wave represents the condition of the ventricle in which the base is in a state of excitation while the apex is as yet unexcited. The T wave has been attributed by some to the arrangement of fibres in the ventricle which is said to be such as to cause the wave of excitation to follow a circular route in the ventricle, the base in one region remaining excited after excitation has ceased at the tip; others have regarded the T wave as the expression of a different process in the muscle—the R wave being the more immediate expression of excitation, the T wave being more intimately linked with the contraction process.

The R and T waves form the usual features of the ventricular complex, the P wave is the only generally recognised sign of auricular excitation in the electrocardiogram. Hering* has recently drawn attention to the existence in certain curves of a second wave in the auricular complex corresponding to the T wave of the ventricular complex. This he has shown by direct derivation both of the mammalian and of the frog's heart. One of my tracings, from a heart in which the ventricle failed occasionally to respond to auricular excitation, shows the second auricular wave unmistakably and gives a suggestion as to why the second auricular wave is not more often seen in the electrocardiogram. In the particular case referred to (fig. 4) the $A—V$ interval at first is short and no second auricular wave is seen. In succeeding beats the $A—V$ interval increases and the second auricular wave (marked with a cross in the figure) appears as a little shoulder on the rise of the R wave. Presently the impulse fails to get through from the auricle to the ventricle, the ventricular complex disappears and the two auricular waves remain, both being in the same direction, the second considerably greater than the first, agreeing with Hering's description. When the $A—V$ interval is of normal duration it would appear that the second auricular wave (Vorhof Ta-Zacke)

* Hering, *Pflüger's Archiv*, 144, p. 1, 1912.

must often escape notice because it is masked by the very much greater *R* wave of the ventricular complex.

If the region under one of the electrodes is injured, the electrogram of the ventricle becomes simplified, as is well known, to a monophasic variation. By perfusion with Ringer's solution it is often possible so far to restore the excitability of the injured region as to lead to conversion of the monophasic into a diphasic record. During the perfusion of the heart with fluid the amplitude of the electrogram is as a rule diminished, no doubt owing to the fact that an additional path for the currents is provided by the solution in the cavity of the heart. As is seen in fig. 5 the effect of the perfusion in restoring the complex form of the electrogram persists after the perfusion has ceased.

Pulsus alternans. In the exposed heart of the frog the condition of *pulsus alternans* occurs not infrequently. The beats follow in normal sequence from auricle to ventricle, but the ventricular contractions are alternately large and small. The electrical record taken from the ventricle in this condition shows alternation, as has been noticed by previous observers. By direct derivation, it often happens that the alternation is much more obvious in the electrical record than in the mechanical. An example, in which the electrogram was monophasic, is given in fig. 6. The continuation of this tracing illustrates the fact that the alternation may often be abolished by treatment with Ringer's solution; in this particular case the treatment did not remove the monophasic character of the electrogram. Sometimes the alternation disappears spontaneously; an instance is given in fig. 7. It will be noticed in this tracing that alternation is scarcely perceptible in the mechanical record, though very marked in the early part of the electrogram. The alternation returned later in this experiment. Figs. 8, 9, 10 show instances from other hearts in which alternation is obvious in the electrical but slight or imperceptible in the mechanical record of the ventricle. The condition in which alternation is revealed by the electrical but not by the mechanical tracing may be called *pulsus alternans celatus.* Like the ordinary condition of *pulsus alternans* it may be abolished by treatment with Ringer's solution or by stimulation of the vagus. *Pulsus alternans celatus* may be regarded as a condition in which the function of a very small portion of the ventricular muscle is upset so that it responds only to every second excitation of the rest of the muscle. The failure of a *very small* part of the muscle to respond to excitation will hardly affect the force of the ventricular systole, yet if situated in certain regions it may modify considerably the form of the electrogram by affecting the path taken by the excitation in the myocardial syncytium. *Pulsus alternans celatus* is probably due to a change in the myocardium similar in nature

to that responsible for *pulsus alternans* but more limited in extent. This is supported by the fact that alternation in the mechanical record commonly appears at a later stage in hearts which have shown *pulsus alternans celatus*. Fig. 11 shows some stages in the onset of *pulsus alternans*. The first portion of the tracing reproduced shows alternation in the electrical but not in the mechanical record. In the second portion it is perceptible in both records: in the third portion it is very striking in both records.

The remarkable similarity between the electrogram of the frog's heart and the human electrocardiogram, both normal and in various conditions of heart block, ectopic beats, *pulsus alternans* and so forth, suggests the possibility that the condition *pulsus alternans celatus* may be encountered in man, in which case it will be of prognostic importance. Lewis* has shown that alternation in the electrocardiogram may exist when none can be detected in the radial pulse, but, so far as I know, the case has not yet been described in which alternation existed in the electrocardiogram with none in the cardiographic *or* radial pulse tracing. The two latter are known to be liable to independent variation, though both are expressions of the mechanical behaviour of the ventricle.

After effects of inhibition on the electrogram.

Samojloff, working on the exposed heart of the frog, found that as a result of stimulation of the vagus the form of the ventricular electrogram underwent a curious change. The R wave was practically unchanged, while the T wave was reduced or reversed in those cases where at the start the T wave was positive (i.e. in the same direction as the R wave). Where the T wave was negative before inhibition (i.e. opposite in direction to the R wave), on recovery from inhibition it became more negative.

I can confirm these conclusions from a number of experiments in which inhibition of the heart was produced by stimulation of the sinus venosus. Fig. 12 shows an instance where the T wave was very markedly cut down. Fig. 13, taken from the same experiment, shows that weaker stimulation, sufficient to cause well-marked slowing of the heart, was not followed by any decided change in the form of the ventricular electrogram. Fig. 14 shows an example in which the T wave, negative at the start, became more negative after inhibition.

In some instances I found that the form of the electrogram remained unchanged even after strong stimulation of the sinus venosus.

Of greater interest is the fact that in a certain number of cases

* Lewis, *Mechanism of the heart beat* (Shaw and Sons), p. 273, 1911. See also H. Frédericq, *Arch. Internat. de Physiol.* 1912, XII. p. 96.

the T wave after inhibition is changed in exactly the opposite sense to that described by Samojloff and confirmed in the experiments to which reference has just been made. In several instances I have found inhibition to be followed by very marked increase in the size of the T wave which remains positive and gradually drops again to its normal amplitude. This I have seen both on stimulation of the sinus venosus and on stimulation of the vago-sympathetic trunk, and with both methods of derivation. An example is shown in fig. 15.

It is evident that any means by which the several parts of the electrogram may be altered independently is important in the interpretation of the complex curves. I propose to defer any discussion as to how far the varying effects of vago-sympathetic stimulation on the electrograms of the frogs' hearts are to be ascribed to differences in arrangement of the muscle fibres in different hearts, how far to differences on the physiological condition of the muscle and as to whether concomitant stimulation of sympathetic fibres plays a part, until the completion of a series of experiments on the tortoise heart.

It is hoped that these experiments will throw light on the relation between the alteration of the electrogram of the beating heart by vagal action and the remarkable electrical effect which Gaskell* demonstrated in 1887 on the quiescent auricle of the tortoise†.

Description of Plates V—IX.

Fig. 1. Frog's heart perfused with Ringer's solution. The top line shows the output of the heart in drops, pumped to a height of 17 cms. Each white patch represents a drop, the length of the patch depends on the time during which the drop hung on the tube before falling. The second line is the shadow of a lever attached to one of the auricles. The third line is from a lever attached to the tip of the ventricle. It is affected in this case also by the auricular movements. The fourth line is the electrogram derived from base and apex of ventricle. Up-stroke in the mechanical records indicates systole; in the electrogram, that the base of ventricle is "zincative" to the apex. The bottom line marks time in seconds. $\times \frac{2}{3}$.

* *Journal of Phys.* VIII. p. 404, 1887.

† Since the above was sent to the Press a paper by Meek and Eyster has appeared (*Amer. Journ. Physiol.* June 1912, XXX. p. 271) in which a repetition of Gaskell's experiment is described, a string galvanometer being used. Meek and Eyster confirm Gaskell's observations in every detail. They point out that the E.M.F. of Gaskell's positive variation is of the order of 10^{-4} volts and that an instrument sensitive enough to register this change in potential is far too sensitive for observations of the relatively enormous potential changes which occur in connexion with heart beats.

Fig. 2. Mechanical records from auricle and ventricle. Electrogram from sinus venosus and apex of ventricle. $\times \frac{2}{3}$.

Fig. 3. Mechanical records as before. Electrogram from base and apex of ventricle. $\times \frac{2}{3}$.

Fig. 4. Mechanical record by suspension of ventricle, showing auricular and ventricular contractions. Up-stroke systole. Electrogram from sinus region and tip of ventricle. Down-stroke of electrogram, in this figure only, indicates base "zincative" to apex. $\times \frac{2}{3}$.

Fig. 5. Mechanical records of auricle and ventricle (up-stroke = systole), electrogram of ventricle. Above the time tracing is a signal line. At start of tracing, heart not perfused. At first signal perfusion with Ringer's solution: at second signal perfusion stopped. $\times \frac{1}{2}$.

Fig. 6. Mechanical records of auricle and ventricle. Down-stroke represents systole. Electrogram of ventricle. *a* shows *pulsus alternans*. *b* after pouring Ringer's solution over the heart. Interval of about a minute between *a* and *b*. $\times \frac{2}{3}$.

Fig. 7. Mechanical records of auricle and ventricle. Down-stroke represents systole. Electrogram of ventricle. The paper moved at the same rate as in the preceding figure. $\times \frac{9}{10}$.

Fig. 8. Mechanical records of auricle and ventricle. Up-stroke represents systole. Electrogram of ventricle. $\times \frac{3}{5}$.

Fig. 9. From same experiment as fig. 8. $\times \frac{3}{5}$.

Fig. 10. Mechanical records of auricle and ventricle. Up-stroke systole. Electrogram of ventricle. $\times \frac{3}{5}$.

Fig. 11. Mechanical record by suspension of ventricle, showing auricular and ventricular beats. Up-stroke systole. Electrogram from base and apex of heart. Interval of about two minutes between *a* and *b* and between *b* and *c*. $\times 1$.

Fig. 12. Mechanical records of auricle and ventricle. Down-stroke systole. Electrogram of ventricle. The break in signal line indicates stimulation of sinus venosus with tetanising current. (Du Bois Reymond coil, secondary at 10 cms., one Daniell in primary.) $\times \frac{3}{7}$.

Fig. 13. From same experiment as fig. 12. Very weak stimulation of sinus venosus during period shown by signal line. $\times \frac{3}{7}$.

Fig. 14. Arrangement as in last two figures. Sinus venosus stimulated. (Secondary coil at 8 cms.) $\times \frac{5}{6}$.

Fig. 15. In mechanical records up-stroke means systole. Electrogram from base and apex of heart. Sinus venosus stimulated. (Secondary coil at 10 cms.) $\times \frac{5}{6}$.

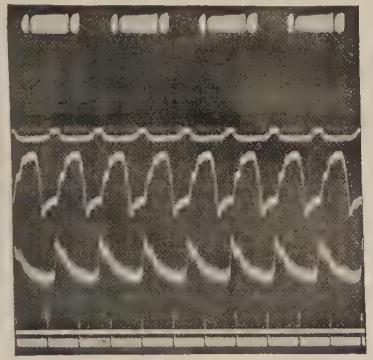
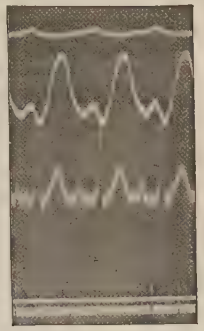


Fig. 1.



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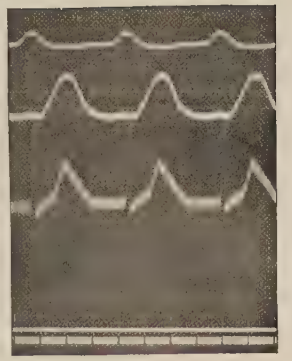

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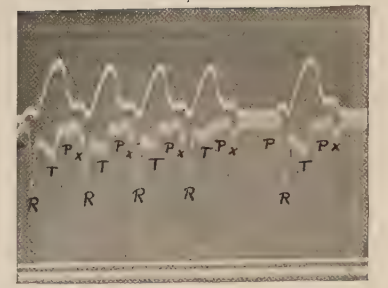

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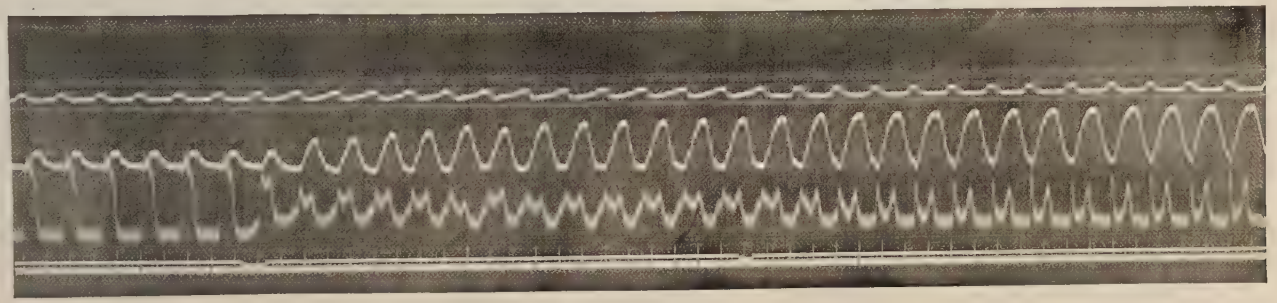

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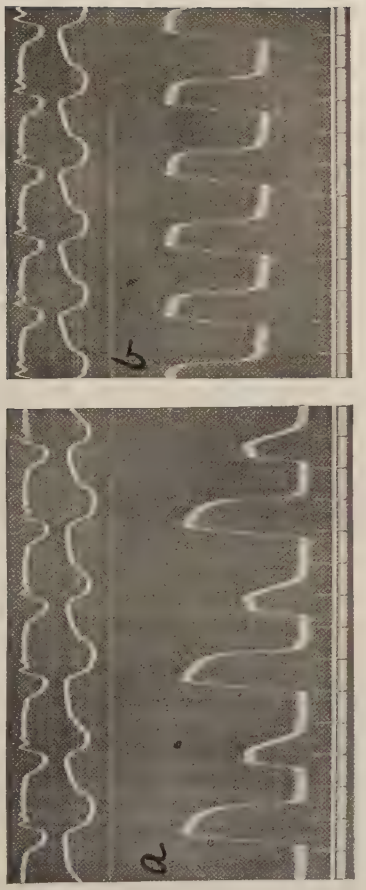

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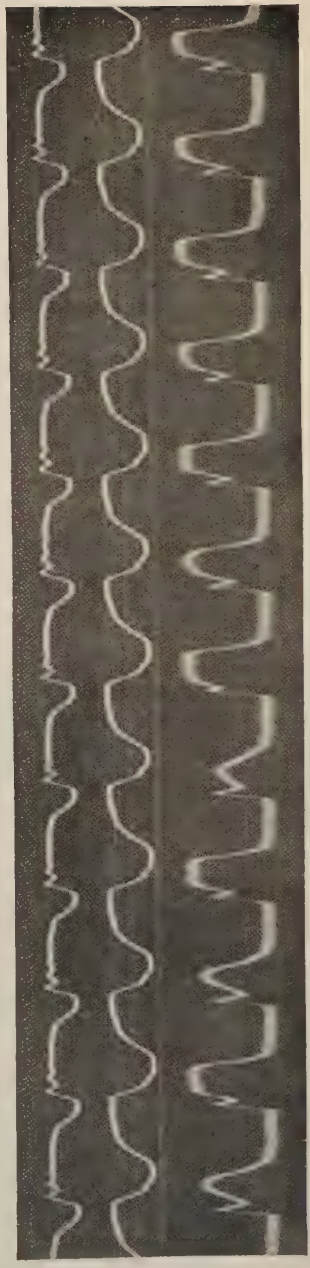


Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

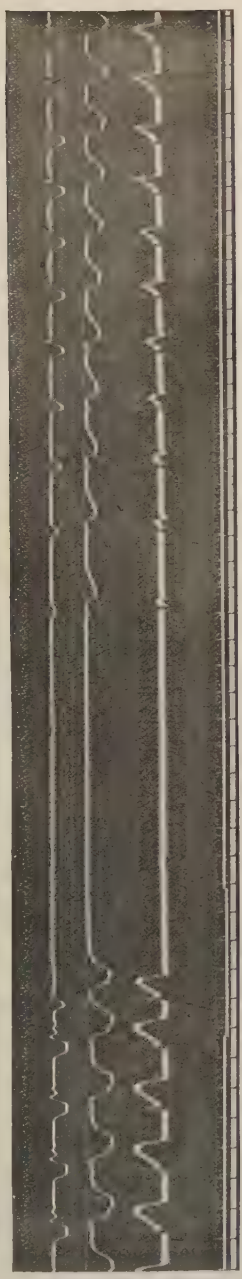


Fig. 12.

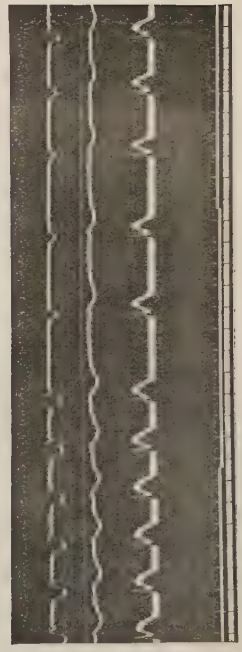


Fig. 13.

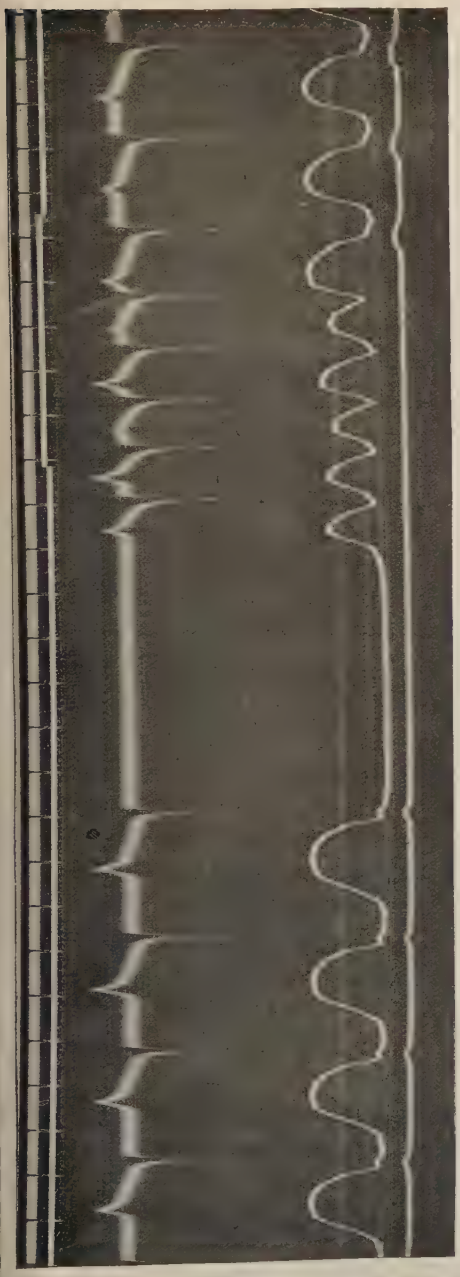


Fig. 14.

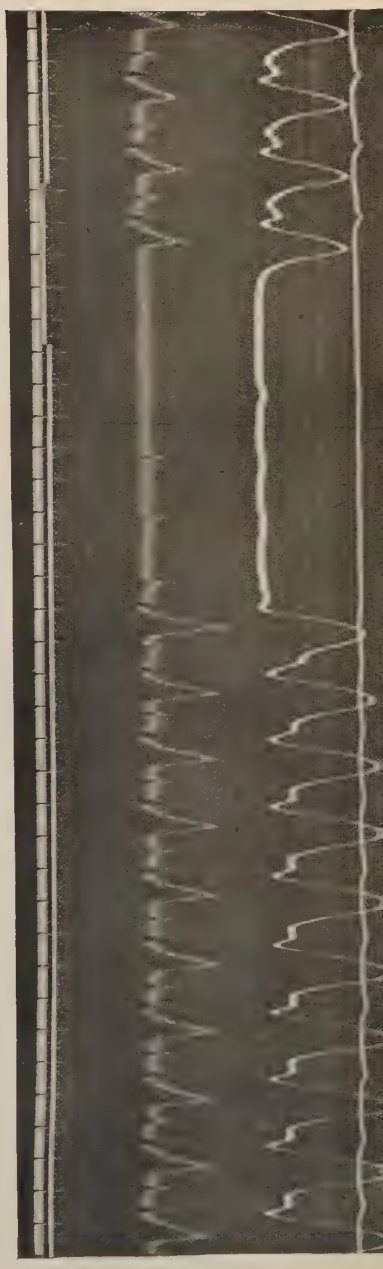


Fig. 15.

On the Ionisation produced by the Collision of Positive Ions in Gaseous Mixtures. By R. D. KLEEMAN, D.Sc. (Adelaide), B.A., Emmanuel College.

[*Received* 30 May 1912.]

A NUMBER of different experiments have been devised with the object of obtaining information on the behaviour and the nature of an ion in a gas under different conditions. But many points remain to be cleared up. This is due to the fact that in a large number of cases the results admit of several explanations equally probable. It is necessary therefore that new methods of attack should be brought to bear on the problems. The writer therefore devised the one described in this paper, which is a modified method of studying the ionisation by collision of ions.

The principle of the method is as follows. A circular wire gauze and metal plate are situated parallel to one another, separated by a distance which is small in comparison with their diameters. The gas on the side of the gauze not facing the metal plate is ionised. By means of a weak electric field the positive or negative ions made can be drawn through the gauze into the space between the gauze and plate. A difference of potential exists between the gauze and plate which may be increased to such a value that ions are produced by collision of the ions pulled through the gauze with the neutral molecules. The current between the gauze and plate is measured by connecting the plate to an electrometer.

In the methods that have usually been used to study the ionisation produced by the collision of ions with neutral molecules the initial ionisation was produced in the powerful field giving rise to ionisation by collision. In such an arrangement the electrons and smallest positive particles produced would be seized upon by the field before they can attach themselves to neutral molecules, and given a large velocity which prevents this taking place later. The ions that are drawn through the gauze are therefore not in the same condition for the production of ionisation by collision as they would be if produced in the powerful electrical field between the gauze and plate. Now the writer has shown* that it follows from the laws of thermo-dynamics and the law of mass action that the nature of an ion cluster in a gas (not under the action of external forces) is continually changing, and a crowd of ions consists therefore at any instant of a number of simple ions (electrons, etc.) and clusters of various

* *Proc. Camb. Phil. Soc.*, vol. XVI. p. 285.

degrees of complexity. Therefore a certain number only of the ions that are drawn through the gauze are in a condition to be used by the powerful electric field for the production of new ions by collision. During the passage of the ions from the gauze to the plate some further ions, however, become simple, and are at once seized upon by the powerful electric field to produce fresh ions.

The shape of the ionisation curves obtained connecting the electric field between gauze and plate with the current passing is regulated by the simple ions of least mass that are drawn through the gauze, for the smaller the mass of the simple ion the weaker the electric field necessary to produce ionisation by collision. By means of the arrangement described it could therefore be tested whether the addition of a small quantity of a gas to the chamber different from that it already contains introduces a new simple ion. A study of the ionisation curves for the positive and negative ions for different gases and mixture of gases was thus likely to lead to interesting and important results.

Fig. 1 is a diagram of the apparatus used in these experiments. A is a cylindrical ionisation chamber 18 cms. long and 12 cms. in diameter. Its electrode a, which consisted of a circular brass plate, was connected with a Dalezalek electrometer through a contact key. A wire gauze b whose meshes were about 1 $(\text{mm.})^2$ in area was situated at a distance from the plate a which was usually ·5 cm. The gauze was soldered to an annular ring c in electrical connection with the chamber; it could be raised or lowered by means of three screws. The inside surface of the annular ring was covered with uranium oxide mixed with a small quantity of liquid gum to make it stick fast to the metal. The portion of the gas in the chamber below the gauze was thus ionised by the α-particles ejected by the uranium into the chamber. When the chamber was connected to a high potential a strong field existed between the gauze and plate, and a comparatively weak field in the same direction between the gauze and lower part of the chamber due to a small fraction of the lines of electric force from the electrode a threading through the gauze and ending on the lower part of the chamber. Therefore when the chamber was at a positive potential, some of the positive ions made by the α-particles of the uranium were drawn through the gauze into the space between gauze and plate, and when at a negative potential some of the negative ions were drawn into this space. Measurements of the leak were carried out for different potentials applied to the chamber.

The chamber was filled with the vapour of a liquid in the following manner. The tap d was closed, the taps e and f were opened and the rubber clips g, h, and i released, and the chamber

exhausted down to as low a pressure as possible by means of a Fleus pump, after which the tap *f* was closed. A small quantity of liquid whose vapour was to be investigated was then poured into the tube *k* of the glass apparatus *B*, and a small quantity of the liquid by opening the tap *d* allowed to run into the bulb *l*. The liquid rapidly evaporated into the chamber *A*, being dried on its way by the drying tube *C* containing phosphorus pentachloride. The remnant of air left in the chamber *A* was forced by the vapour into the chamber *D*, whose capacity was about eight times that of *A*. The evaporation of the liquid was usually allowed to go on till the vapour pressure was a few cms. of mercury, and the clips *g* and *i* then tightened, cutting off the communication of the chamber *A* with *B*, *D*, and *C*. The pressure of the vapour in the chamber, indicated by the mercury gauge *F*, was then reduced to any desired

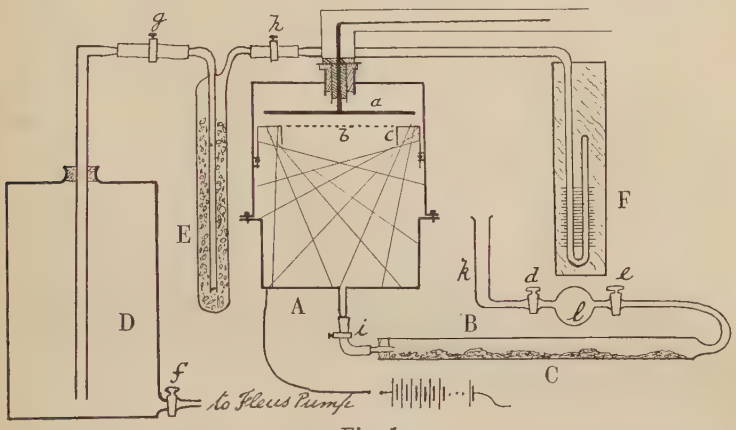


Fig. 1.

magnitude by immersing the tube *E* in liquid air. The tube contained cocoa-nut charcoal, and a lowering of its temperature caused a gradual absorption of vapour by the charcoal. When the vapour pressure had decreased down to the desired magnitude, the communication between the tube and chamber was cut off by tightening the clip *h*. The apparatus was now ready for carrying out the electrical measurements.

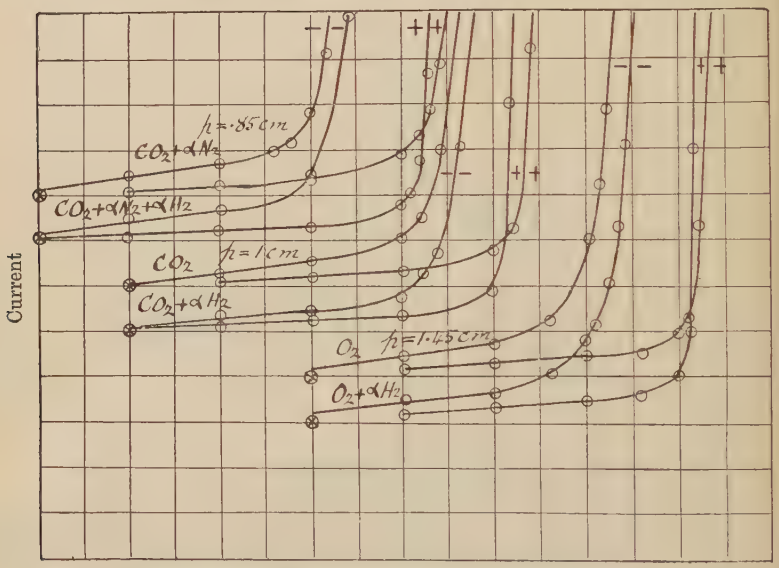
The vapour in the chamber at the end of a set of measurements was removed by a current of dry air. The vapour occluded by the charcoal was removed by exhausting the tube for some time during which it was placed in the hot air of a bunsen flame.

When a small quantity of a gas was added to the gas the chamber already contained, it was first passed into a thin glass tube about 6 cms. long having a very small hole at each end. A rubber tube fitted over one end of the glass tube, which was

clipped after the tube had been filled with the gas required. The other end of the glass tube was then fitted into a very short rubber tube in connection with the chamber and communication between the glass tube and chamber then established.

In this paper we will deal principally with the ionisation curves obtained with the positive ion, and the effect produced on their shape by adding a small quantity of gas into the chamber different from that it already contained.

Let us consider the effect the addition of a small quantity of gas to that contained by the chamber would have on the shape of the ionisation curve. The general nature of an ionisation curve



Electric field, one division being equal to 40 volts

Fig. 2.

connecting the electric field between gauze and plate with the current passing will appear from an inspection of the curves in figures 2, 3, 4, 5, and 6. Roughly a curve may be divided into two lines, a horizontal and vertical line, the beginning of the latter showing where the ionisation by collision begins to come in. Let us first consider the case when the nature of the simple ion is independent of the nature of the gas in which it is produced; in the case of the negative ion it would always be the electron carrying a charge *e*. The total number of ions drawn through the gauze would be slightly increased after the addition of a small quantity of gas. Further, the proportion of simple to complex

ions may be changed to some extent, since the stability of a cluster depends on the nature of the molecules it contains. This will affect the shape of the curve since it depends on the magnitude of the initial ionisation; an increase of the initial ionisation shifts the vertical part of the curve towards the zero, as will be readily seen on doubling the ordinates of one of the curves in fig. 2. But it will make the vertical part of the curve appear less steep. But this effect must be small in comparison with that due to a decrease in the mean free path of the simple ion on addition of the gas. This has the effect of shifting the vertical part of the curve away from the zero, since a larger field is now

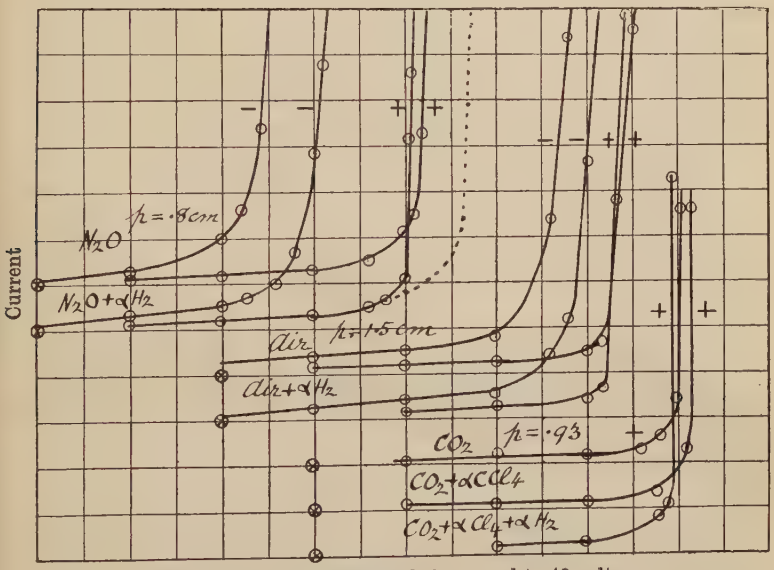


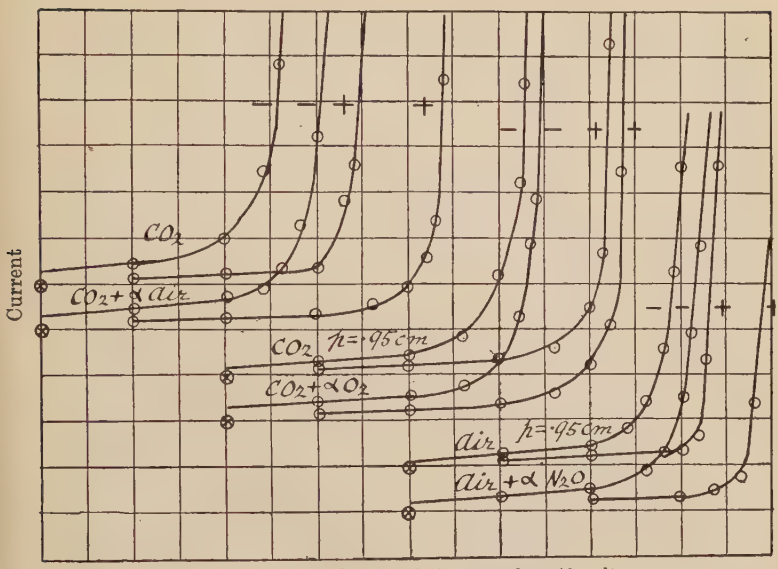
Fig. 3.

necessary to produce ionisation by collision. Now this was found to happen invariably when fresh ions were produced by the collision of negative ions. This is shown by the curves in figures 2, 3, 4, 5, and 6. Each curve obtained by the negative ion is indicated by the sign – placed beside it, and each curve obtained by the positive ion by the sign +. The upper curves were obtained with pure gases, and the lower ones with an admixture of a small quantity of a different gas. A mixture of this kind is denoted in general by $A + \alpha B$, indicating that a small quantity of the gas B is mixed with A. They are plotted to different zeros, each being indicated by a cipher with a cross in the centre.

From the foregoing results we would expect that if the mass of the simple positive ion is independent of the nature of the gas in which it is made, the addition of a small quantity of a gas should produce a similar effect as in the case of the negative ion. This was found, however, not to be the case. When a small quantity of hydrogen was added to one of the gases carbon dioxide, nitrous oxide, oxygen, nitrogen, the vertical part of the curve instead of being shifted away from the zero was shifted towards it. Moreover, the curve was usually rendered more steep. This is shown by the curves in figures 2 and 3. The effect is much more pronounced than one is led at first sight to infer from the curves. If the behaviour of the positive ion were normal the positive curve would be shifted away from the zero approximately to the same extent as the negative, as indicated in one case in fig. 3 by a dotted curve. The total effect produced thus consists in the positive curve being shifted back to its previous position, and in addition to a certain extent further towards the zero. It is difficult to see how the effect could be produced by a change in the proportion of simple to complex ions of those drawn through the gauze. This proportion would be dominated by the clusters of greatest stability. The introduction of a gas which gives rise to additional kinds but less stable clusters would therefore not alter matters much. Moreover the change thus introduced would have to be large to account for the effect. It appears, therefore, bearing also the experiments on the negative ions in mind, that the effect is due to the introduction of a different simple positive ion of smaller mass than that made from the gas the chamber already contains.

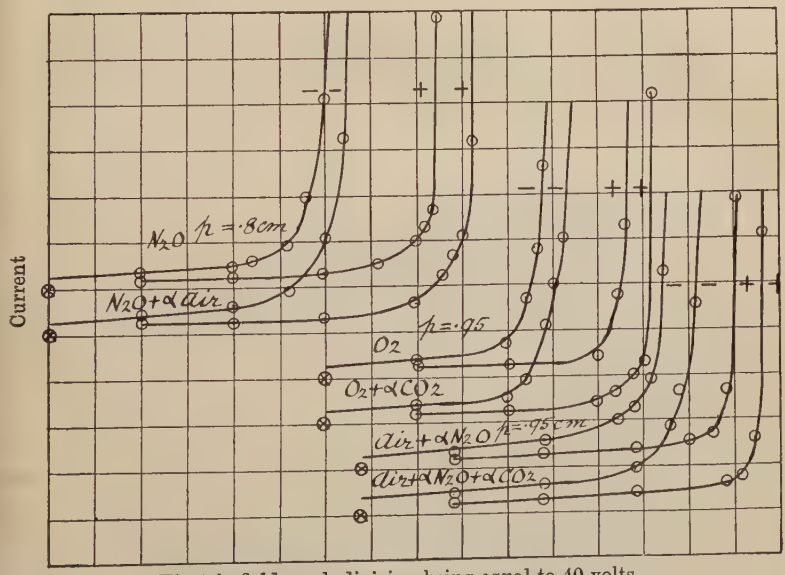
It might perhaps be suggested that the effect could be explained by supposing that ions are produced more easily by collision from hydrogen (H_2) than from the other gases. But the results obtained in experiments on the ionisation by the α-particle are against this view. The writer* has calculated the relative energies necessary to make an ion from different atoms by the α-particle, from which it appears that the largest amount of energy is necessary in the case of an atom of hydrogen occurring in (H_2). Moreover, if the above explanation were true it would probably also apply to the negative ion, and the curve for the negative ion would be shifted towards the zero as is the case with the curve for the positive ion. But this, we have seen, does not happen. It may also be mentioned that the experiments on the total ionisation produced in the different gases by the cathode rays ejected by X-rays do not show that hydrogen is more easily ionised than other gases†.

* *Proc. Roy. Soc.*, Ser. A, pp. 220—233, May 14, 1907.
† *Ibid.*, Ser. A, Vol. LXXXIV. p. 16, June 9, 1910.



Electric field, one division being equal to 40 volts

Fig. 4.

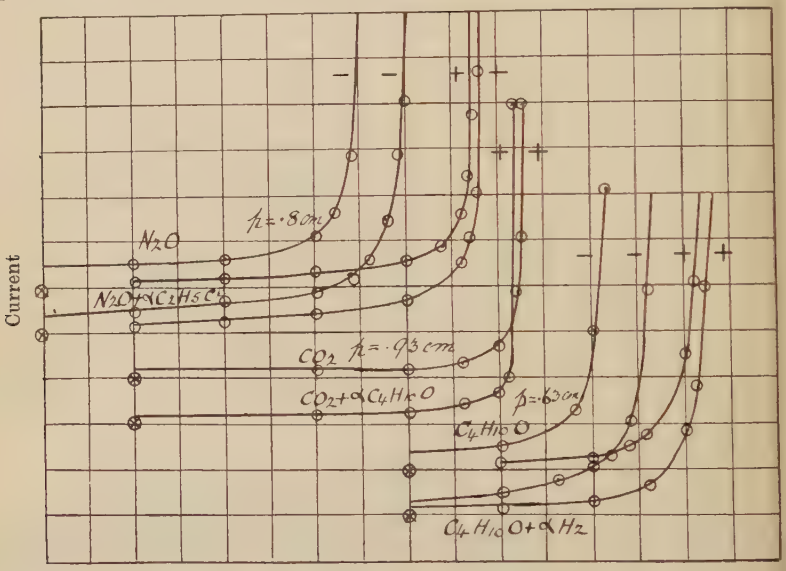


Electric field, each division being equal to 40 volts

Fig. 5.

It was found that no such effect was obtained if the molecules of the gas added consisted of atoms each of whose weight was approximately equal to that of an atom of a molecule of the gas already in the chamber. This is shown by the curves in figures 4 and 5.

It appears therefore that the smallest positive particle that can be obtained from an ionised atom is characteristic of it, and therefore consists probably of the whole atom positively charged. It should, however, be pointed out that the same effect would be obtained if the mass of the simple positive ion is the same in all gases, but that in some cases it carries a larger positive charge



Electric field, each division being equal to 40 volts

Fig. 6.

than in others. But experiments on the charge carried by the positive ions made by the α-particle in different gases show that it is of the same magnitude as that carried by the negative ions, *i.e.* a single charge e.

It became of interest next to test whether the addition of a small quantity of a gas to the chamber whose molecules contain a number of hydrogen atoms besides other atoms produces the same effect as adding hydrogen. Evidence was obtained that they produce the same effect. This is shown by curves in fig. 6. It will be seen that the addition of a small quantity of gaseous ether to carbon dioxide gas shifts the curve for the positive ion towards the zero, as occurs on adding hydrogen. The addition of

a small quantity of ethyl chloride gas to carbon dioxide, in the experiment carried out, did not shift the curve for the positive ion towards zero but slightly in the other direction, which is, however, small in comparison with the extent the curve for the negative ion was displaced. It seems that the amount of hydrogen introduced per molecule of ethyl chloride is not sufficient to compensate for the increase produced by the molecule in the mean free path of the + ion. The experiments are tedious to carry out, and the quantity of ethyl chloride gas necessary to shift the curve towards zero, an effect foreshadowed by the curves in the figure, was therefore not investigated. The results indicate that when an atom of a molecule is ionised by an α-particle the whole molecule may sometimes be broken up into its constituent atoms. There is other evidence that such a thing very likely happens. It has been observed that various gases, principally hydrogen and oxygen, are gradually formed in a closed chamber containing radium. This has been supposed to be due to the decomposition of the moisture by the rays from the radium.

If the foregoing explanation is true, then the addition of hydrogen to a gas whose molecules contain atoms of hydrogen should not have the same effect as previously, but the curve for the positive ion should be shifted away from the zero. The gas initially in the chamber would in this case already contain free positive hydrogen ions, and the addition of hydrogen, which gives rise to the same kind of ion, would therefore shift the curve away from the zero as we have seen happens in the combination of gases whose curves are given in figures 4 and 5. An experiment carried out with ether showed that this is the case, the curves obtained being shown in fig. 6.

The experiments carried out by various observers on the mass of the positive ion in a discharge tube, especially those by Sir J. J. Thomson, should be mentioned in connection with the results described in this paper. In these experiments a stream of positive particles moving with a high velocity is subjected to a magnetic and electric field at right angles to one another, and the deviation of the particles from their paths made visible by allowing them to fall on a Willimite screen. A number of bright spots are usually obtained, indicating the existence of positive particles of different masses. Sir J. J. Thomson in one of his papers* showed that the spot due to hydrogen was increased in brightness when a small quantity of gas was added whose molecules did not contain hydrogen atoms. The experiments seemed to show that the nature of the simple positive ion was independent of the nature of the gas in which it was made, and consisted of the hydrogen atom positively charged. But there is an important point that

* *Phil. Mag.*, May 1907, pp. 561—575.

has to be taken into account in this connection. It was mentioned in a previous part of this paper that the ion is not stable at constant temperature, but goes through a series of changes involving clusters of different complexities having different periods of life. In a discharge tube the period of life of a cluster is usually larger than the time it takes to cross the tube, and it is therefore possible to obtain evidence of its existence. From the investigation given in connection with the process of change in clustering of an ion it will appear that the variety and number of different clusters that fall on the screen are regulated by a number of different factors. Thus when the mean free path of a cluster becomes comparable with the dimensions of the tube the number of sets of different clusters and the number of clusters in each set depend on the dimensions of the tube and the pressure of the gas it contains. Further, the addition of another gas to the tube may have the effect of increasing the intensity of a spot on the screen due to a gas which does not contain the same kind of atoms as the gas added. The relative proportion of the different clusters or charged molecules in a gas, in the composition of which a number of different atoms enter, is regulated by the laws of thermo-dynamics and the law of mass action when the volume of the gas is large in comparison with the mean free path of a cluster. When this is no longer the case the dimension of the volume of the gas enters as another factor. The addition of another gas to the tube changes the conditions of equilibrium which may result in an increase in the proportion of one or more of the gases. It will be evident therefore that the experimental result quoted may be explained in more ways than one.

Sir J. J. Thomson after further perfecting the method of investigation obtained evidence that the atom can be positively charged without having a positively charged body of the mass of a hydrogen atom attached to it. But in all these experiments hydrogen atoms positively charged were present in the tube. Two possible explanations of the results present themselves: viz., that the smallest positive particle that can be obtained from an atom is the atom minus a negative electron; or, that the smallest positive particle is the hydrogen atom minus an electron, but which is not always separated from its parent atom during ionisation. If the explanation given of the experimental results described in this paper is the correct one the former explanation has to be adopted.

In conclusion I wish to thank Professor Sir J. J. Thomson for his interest in these experiments. I should also mention that part of the apparatus used was purchased out of a research grant from the Royal Society.

On the Properties of Substances connected with the Kinetic Properties of the Molecules. I. By R. D. Kleeman, B.A (Emmanuel College), D.Sc. (Adelaide).

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In a previous paper* the writer has deduced general formulae for the coefficient of viscosity, conduction of heat, etc., of a substance. In this paper the formulae will be considered in greater detail, and further applications to the facts given.

The Radius of the Sphere of Action of a Molecule in a Pure Substance.

In the paper mentioned it is shown that the viscosity η of a pure substance is given by the equation

$$\eta = l_1 n_1 m_{a1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

where l_1 denotes the mean free path of a molecule, m_{a1} its absolute mass, and n_1 the number of molecules crossing 1 cm.^{2} at right angles in one direction per second which is equivalent to the number actually crossing the cm.^{2} in one direction at all angles. For the exact definition of the mean free path of a molecule in the case of viscosity the paper mentioned must be consulted.

The quantity n_1 is given by the equation

$$n_1 2{\cdot}534 \times 10^{-20} \sqrt{T m_1} = P_n + p \quad \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where m_1 is the mass of a molecule relative to that of a hydrogen molecule, p is the external pressure and P_n the intrinsic pressure of the liquid. The value of P_n is approximately given by

$$P_n = \frac{T\alpha}{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3),$$

and by

$$P_n = L_1 \rho \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4),$$

where α denotes the coefficient of expansion with rise of temperature, β the coefficient of compression at the constant temperature T, ρ the density of the substance, and L_1 the energy necessary to separate the molecules of a gram of substance by an infinite distance from one another. At low temperatures L_1 is the internal heat of evaporation.

The value of l_1 has been calculated† in the case of a few liquids by means of equations (1), (2), and (3).

The effect of the attraction of the molecules on one another and their actual volume on their mean free path may conveniently

* *Phil. Mag.*, July 1912, pp. 101—118.

† *Loc. cit.*

be supposed to be the result of each molecule consisting of a sphere of attractionless matter which produces the same effect as the molecular attraction and the actual volume. The radius σ_1 of this sphere may be called the radius of the sphere of action of the molecule. It is connected with the mean free path of the molecule by the equation

$$l_1 = \frac{3}{16\pi N_1 \sigma_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5),$$

where N_1 denotes the number of molecules in a c.c. The values of σ_1 are given for a few liquids in Table I, using the values of l_1 found previously, N_1 being given by the equation $N_1 = \frac{\rho}{m_{a1}}$, taking the absolute mass of a hydrogen atom equal to $1{\cdot}61 \times 10^{-24}$ grm.

TABLE I.

Substance	t	ρ	l_1	σ_1
Benzene	0	·9001	$7{\cdot}02 \times 10^{-8}$ cms.	$1{\cdot}09 \times 10^{-8}$ cms.
Chloroform.....	0	1·5264	4·14 „	·442 „
Methyl Isobutyrate	18·2	·8891	4·59 „	1·54 „

The values are smaller than those obtained from viscosity data when the molecules are in the gaseous state. This shows that the apparent radius of a molecule is largely due to the field of force surrounding it. Thus when the density of a substance is so great that the molecules are considerably under the influence of each other's attraction, the effect of one molecule on another is to a certain extent neutralized by the other molecules, which produces a decrease in the value of σ_1 from that obtained when the molecules are in the gaseous state.

A Property of the Coefficient of Viscosity.

On combining equations (1) and (2), we obtain the equation

$$\eta = \frac{l_1 m_{a1} (P_n + p)}{2{\cdot}534 \times 10^{-20} \sqrt{T m_1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

In previous papers* the writer has shown that $P_n = k_1 p_c$, and $p = k_2 p_c$, where p_c denotes the critical pressure, and k_1 and k_2

* *Phil. Mag.*, Oct. 1910, p. 668; *Phil. Mag.*, March 1911, p. 337; *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vi. p. 546.

quantities which have the same values for all substances at corresponding states. It is not unlikely that also

$$l_1 = k_3 l_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7),$$

where l_c denotes the mean free path of a molecule at the critical point, and k_3 a quantity which has the same value for all substances at corresponding states. Equation (6) could then be written

$$\eta = k_4 \frac{l_c p_c m_1^{\frac{1}{2}}}{T_c^{\frac{1}{2}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8),$$

where k_4 has the same value for all substances at corresponding states. According to this equation the ratio $\frac{\eta_1}{\eta_2}$ should be the same for all liquids, where η_1 and η_2 refer to two corresponding temperatures. This is tested in Table II for a number of liquids, the

TABLE II.

t	η_1 and η_2	η_1/η_2	t	η_1 and η_2	η_1/η_2	t	η_1 and η_2	η_1/η_2
Ethelene-bromide, $C_4H_4Br_2$			Ethelene-chloride, $C_4H_4Cl_2$			Propyl acetate, $C_5H_{10}O_2$		
18·4	·01767	1·770	7·7	·01000	1·693	1·6	·007638	1·693
60	·009985		47·8	·005903		40·8	·00451	
Ethyl propionate, $C_5H_{10}O_2$			Methyl butyrate, $C_5H_{10}O_2$			Methyl isobutyrate, $C_5H_{10}O_2$		
−3	·007040	1·822	2·5	·00734	1·657	·3	·007011	1·686
38·6	·003864		41·9	·00443		39·3	·004160	
Thiophen, C_4H_4S			Benzene, C_6H_6			Toluol, C_7H_8		
22·1	·00644	1·579	3·8	·008680	1·831	23·9	·00560	1·555
64·3	·00408		43·3	·004740		66·3	·00360	
Ethyl benzene, C_8H_{10}			Propionic acid, $C_3H_6O_2$			Butyric acid, $C_4H_8O_2$		
36·7	·00550	1·540	33·4	·009169	1·635	32·5	·01255	1·777
80·9	·00357		77·2	·005605		76·1	·007016	
Octane, C_8H_{18}			Carbon tetrachloride CCl_4			Alcohol, C_2H_6O		
11·6	·006060	1·603	5	·0124	1·781	30·5	·009895	1·750
52·2	·003783		44·7	·00696		74	·005654	

values of η_1 and η_2 corresponding to the temperatures $\frac{T_c}{2}$ and $\frac{T_c}{7}$ respectively. It will be seen that the ratio is roughly constant, showing that the condition expressed by equation (7) is at least approximately satisfied.

Although in the case of a liquid the mean free paths of a molecule which occur in viscosity, conduction of heat, and diffusion are not equal to one another*, yet on account of their similar nature each probably obeys the condition expressed by equation (7).

The Average Velocity of a Molecule in a Pure Substance.

The velocity of a molecule in a substance is continually changing, due to the attraction of the molecules upon one another, the effect being increased with an increase of density of the substance. When the molecule passes through a point at which the forces of the surrounding molecules neutralize one another, its velocity is equal to that which it has in the gaseous state at the same temperature†. But the average velocity is much greater than this velocity‡. It will be of interest therefore to obtain a formula for the average velocity of a molecule in a substance.

Suppose a molecule undergoes a displacement x in any given direction. Energy is expended upon it due to the attraction exerted by the surrounding molecules. The attraction between two molecules is given by $\phi\left(\frac{T}{T_c}, \frac{x_c}{z}\right).\frac{(\Sigma\sqrt{m_1'})^2}{z^5}$ or $(\phi).\frac{(\Sigma\sqrt{m_1'})^2}{z^5}$, where z denotes the distance of separation of the molecules, x_c the distance of separation of the molecules of the substance in the critical state, T the temperature and T_c the critical temperature, and $\Sigma\sqrt{m_1'}$ the sum of the square roots of the atomic weights of the atoms of a molecule. The change in the kinetic energy of the molecule due to the attraction of one of the surrounding molecules is therefore $\int_{nx_a}^{wx_a}(\phi).\frac{(\Sigma\sqrt{m_1})^2}{z^5}.dz$, where wx_a is their distance of separation before and nx_a after the displacement, x_a denoting the distance of separation of the molecules of the substance. The total change in kinetic energy of the molecule due to the attraction of the surrounding molecules is therefore

$$\sum_{w=a}^{w=\infty}\int^{wx_a}(\phi).\frac{(\Sigma\sqrt{m_1'})^2}{z^5}.dz - \sum_{n=b}^{n=\infty}\int^{nx_a}(\phi).\frac{(\Sigma\sqrt{m_1'})^2}{z^5}.dz.$$

* *Loc. cit.*
† *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vi. pp. 540—542.
‡ *Phil. Mag.*, July 1912, pp. 102, 103; *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vii.

This expression may be written $\psi_1\left(\frac{T}{T_c}, \frac{x_c}{x_a}\right).\frac{(\Sigma\sqrt{m_1'})^2}{x_a^4}$. Since $x_a=\left(\frac{m_{a1}}{\rho}\right)^{\frac{1}{3}}$, it may also be written $K_1\left(\frac{\rho}{m_a}\right)^{\frac{4}{3}}(\Sigma\sqrt{m_1})^2$, where K_1 has the same value for all substances at corresponding states.

It can be shown that all the possible displacements a molecule can undergo in substances at corresponding states are the same fractions and multiples of the distances of separation of the molecules, or, the possible values of n and w are the same for substances at corresponding states. The molecules of a substance at the absolute zero have no motion of translation and are therefore in contact with one another. The actual volume a molecule occupies is thus equal to that it occupies at the absolute zero, or at least proportional to it. In substances at corresponding states it is thus proportional to the apparent molecular volume. Thus the fraction of the total volume of the substance available for motion of the molecules is the same for substances at corresponding states, and the above statement then at once follows.

Let us consider two liquids at corresponding states at an instant when the molecules are similarly situated with respect to one another in each case. Consider a molecule in each liquid which is similarly situated in respect to the surrounding molecules, that is, so that each is situated at distances from the surrounding molecules given by $\sum_{n=a}^{n=b} nx_a$. The component of motion of each molecule representing its temperature energy is in the same direction with respect to the situation of the surrounding molecules. This kinetic energy is equal to T. The component of motion representing the kinetic energy due to the attraction of the surrounding molecules is also in each case in the same direction with respect to the surrounding molecules. The kinetic energy in the latter case, from what has gone before, is equal to $K_3\left(\frac{\rho}{m_{a1}}\right)^{\frac{4}{3}}(\Sigma\sqrt{m_1'})^2$, where K_3 has the same value for all substances at corresponding states. Now in previous papers* we have shown that

$$T=H^2\left(\frac{\rho}{m_1}\right)^{\frac{4}{3}}(\Sigma\sqrt{m_1'})^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9),$$

where H^2 has the same value for all substances at corresponding states. The foregoing expression may therefore be written aT, where a has the same value for all substances at corresponding states. It follows therefore that the direction of motion of the resultant kinetic energy is in the same direction with respect to

* *Phil. Mag.*, Oct. 1909, p. 509; and May 1910, p. 787.

the surrounding molecules in both cases, and equal to bT, where b has the same value for all substances at corresponding states. It follows therefore that the average velocity of a molecule is the same multiple of the velocity of a molecule in the gaseous state in all substances at corresponding states. Further, if V_1 denote the average velocity of a molecule 1, and V_{t1} that corresponding to its temperature, we have

$$V_1 = k_5 \frac{\rho^{\frac{2}{3}}}{m_1^{\frac{7}{6}}} \Sigma \sqrt{m_1'} \quad \text{.....(10),}$$

and

$$V_{t1} = a_1 \left(\frac{T}{m_1}\right)^{\frac{1}{2}} = k_6 \frac{\rho^{\frac{2}{3}}}{m_1^{\frac{7}{6}}} \Sigma \sqrt{m_1'} \quad \text{.....(11),}$$

where k_5 and k_6 have the same value for all substances at corresponding states.

A Radius of the Sphere of Action of a Molecule from the Equation of State.

In a paper written previously to this (which has not yet appeared in print) it is shown that the equation of state may be written in the form

$$p + P_n = \frac{V_1}{V_{t1}} \frac{RT}{m_1(v_1 - 16\pi W_{11} w_1^2/3m_{a1})} \quad \text{.....(12),}$$

where V_1 denotes the average velocity of a molecule, V_{t1} that corresponding to the temperature in the gaseous state, v_1 the volume of a gram of substance, w_1 the actual radius of a molecule, and W_{11} the radius of the sphere of action of a molecule which gives rise to actual collision between two molecules*. Now in a previous paper† we have shown that

$$P_n = K_2 \left(\frac{\rho}{m_1}\right)^{\frac{7}{3}} (\Sigma \sqrt{m_1})^2 \quad \text{.....(13),}$$

and

$$p = M^2 \left(\frac{\rho}{m_1}\right)^{\frac{7}{3}} (\Sigma \sqrt{m_1})^2 \quad \text{.....(14),}$$

where K_2 and M^2 have the same value for all substances at corresponding states. On substituting the values of P_n, p, V_1, V_{t1}, and T, given by the equations (13), (14), (10), (11), and (9), in equation (12), we see that it may be written

$$W_{11} w_1^2 = F_1 \frac{m_1}{\rho} \quad \text{.....(15),}$$

* The equation can be established in the same way as an equation in the last section of this paper.

† *Loc. cit.* and *Phil. Mag.*, Dec. 1909, p. 903, and May 1910, p. 788.

where F_1 is the same for all substances at corresponding states. We may therefore write

$$w_1 = F_3\left(\frac{m_1}{\rho}\right)^{\frac{1}{3}} \quad \text{.....(16),}$$

and

$$W_{11} = F_2\left(\frac{m_1}{\rho}\right)^{\frac{1}{3}} \quad \text{.....(17),}$$

where F_2 and F_3 have the same value for all substances at corresponding states. The radius w_1 is not equal to the radius σ_1, but is smaller; the ratio of the two should, however, be constant.

The value of W_{11} given by equation (17) applies only to a substance of such a density that the term $16\pi W_{11} w_1^2/3m_{a1}$ is not negligible in comparison with v_1 in equation (12). The value of σ_1, which is proportional to W_{11}, for substances of less density than that, will be investigated in the next section.

A Mean Free Path and a Radius of the Sphere of Action of a Molecule from Maxwell's Equation.

If the molecules in a gas are regarded as centres of force, and two molecules attract one another according to the law $\frac{B}{z^5}$, where z denotes their distance of separation, and B a constant depending on their nature, the coefficient of diffusion δ_{12} of molecules 1 in molecules 2 is given according to Maxwell by

$$\delta_{12} = \frac{p_1}{\rho_1} \frac{p_2}{\rho_2 A \left\{\frac{B}{m_1 m_2 (m_1 + m_2)}\right\}^{\frac{1}{2}}} \frac{1}{p} \quad \text{.....(18),}$$

where p_1, ρ_1, p_2, ρ_2 are the partial pressures and densities of the molecules 1 and 2 respectively and m_1 and m_2 the molecular weights and $p = p_1 + p_2$. From previous work it appears that the attraction between two molecules 1 and 2 is approximately given by $G_1 \frac{\Sigma\sqrt{m_1'}\,\Sigma\sqrt{m_2'}}{z^5}$, where G_1 is a function of the temperature, and $\Sigma\sqrt{m_1'}$ denotes the sum of the square roots of the atomic weights of the atoms of molecules 1, and $\Sigma\sqrt{m_2'}$ has a corresponding meaning. If the number of molecules 1 is small in comparison with the number of molecules 2 the above equation becomes

$$\delta_{12} = \frac{G_2}{N_2} \left\{\frac{m_1 + m_2}{m_1 m_2 \Sigma\sqrt{m_1'}\,\Sigma\sqrt{m_2'}}\right\}^{\frac{1}{2}} \quad \text{.....(19),}$$

where G_2 is a function of the temperature and N_2 is the concentration of the molecules 2. The coefficient of diffusion calculated from this equation agrees well with the facts*.

From the kinetic theory of gases we have

$$\delta_{12} = l_{12} V_1 = l_1 \left(\frac{3RT}{m_1}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (20),$$

if the number of molecules 1 is small in comparison with the number of molecules 2, where l_{12} denotes the mean free path of a molecule 1 and V_1 its velocity of translation. Equating the values of δ_{12} given by equations (19) and (20) we obtain

$$l_{12} = \frac{G_3}{N_2} \left\{\frac{m_1 + m_2}{m_2 \Sigma \sqrt{m_1'} \Sigma \sqrt{m_2'}}\right\}^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (21),$$

where G_3 is a function of the temperature. The ratio of the mean free paths l_{12} and l_{32} of a molecule 1 and 3 is therefore given by

$$\frac{l_{12}}{l_{32}} = \left\{\frac{m_1 + m_2}{m_3 + m_2} \frac{\Sigma \sqrt{m_3'}}{\Sigma \sqrt{m_1'}}\right\}^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (22).$$

The mean radius σ_{12} of the sphere of action of a molecule 1 and 2 is given by $l_{12} = \dfrac{3}{16 N_2 \pi \sigma_{12}^2}$, or

$$\sigma_{12} = \left(\frac{3}{16\pi G_3}\right)^{\frac{1}{2}} \left\{\frac{m_2 \Sigma \sqrt{m_1'} \Sigma \sqrt{m_2'}}{m_1 + m_2}\right\}^{\frac{1}{4}} \quad \ldots\ldots\ldots\ldots (23).$$

This equation holds independently of the relative densities of the molecules 1 and 2. The ratio of σ_{12} to σ_{32} is given by the equation

$$\frac{\sigma_{12}}{\sigma_{32}} = \left\{\frac{m_3 + m_2}{m_1 + m_2} \frac{\Sigma \sqrt{m_1'}}{\Sigma \sqrt{m_3'}}\right\}^{\frac{1}{4}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (24).$$

When the molecules in a substance are all of the same kind, say of 1, the law of attraction between two molecules is

$$(\phi) \frac{(\Sigma \sqrt{m_1'})^2}{z^5}.$$

The function (ϕ), which may be taken approximately a function of the temperature only†, has the same value for all substances at corresponding states. The quantities G_2 and G_3 in equations (19) and (21) are then equal to $\dfrac{aT}{(\phi)^{\frac{1}{2}}}$ and $\dfrac{bT^{\frac{1}{2}}}{(\phi)^{\frac{1}{2}}}$ respectively, where a and b are numerical constants. Equation (21) then becomes

$$l_1 = \frac{bT^{\frac{1}{2}}\sqrt{2}}{N_1 (\phi)^{\frac{1}{2}} \Sigma \sqrt{m_1'}} = \left(\frac{\rho}{m_1}\right)^{\frac{2}{3}} \frac{bH\sqrt{2}}{N_1 (\phi)^{\frac{1}{2}}} = \frac{G_4}{N_1} \left(\frac{\rho}{m_1}\right)^{\frac{2}{3}} \ldots (25),$$

* *Phil. Mag.*, May 1910, pp. 806—807.

† *Proc. Camb. Phil. Soc.*, Vol. xvi. Pt vi. p. 555.

by the help of equation (9), where G_4 has the same value for all substances at corresponding states. It follows therefore that

$$\sigma_1 = F_2\left(\frac{m_1}{\rho}\right)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(26),$$

where F_2 has the same value for all substances at corresponding states. This equation is the same in form as equation (17). It appears therefore that each holds in general, that is, applies to matter of any density; and that this probably also applies to equations (21) and (23). We shall obtain results in a subsequent paper showing that this is the case.

The Nature of the Constant in the Viscosity Equation.

By means of equations (26) and (5) we can give equation (8) a more convenient form. It may now be written

$$\eta = k_7 \frac{\rho_c^{\frac{2}{3}} p_c}{T_c m^{\frac{1}{6}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(27),$$

where k_7 has the same value for all substances at corresponding states. This equation is tested in Table III, which contains the

TABLE III.

Substance	η (Exper.)	η (Calc.)
Methyl butyrate ...	·00734	·00829
Benzene	·00868	·008602
Heptane.....	·005367	·006615
Octane	·00606	·006655
Carbon tetrachloride	·0124	·01169
Ethelene-bromide ...	·01767	·01734

values of η for a few substances corresponding to the temperature $\frac{T_c}{2}$, and the values of the right-hand side of equation (27) putting $k_5 = 7{\cdot}59 \times 10^{-5}$. The value of ρ_c in the case of ethelene bromide was calculated by means of the equation $p_c = \frac{RT_c\rho_c}{3{\cdot}7\, m_1}$. The agreement between the two sets of values is very good. This is further evidence that equation (26) holds approximately in general.

The Nature of the Temperature Function in the Viscosity Equation.

It is of importance next to obtain an expression for k_5 in equation (27). This can be done by the help of some theoretical investigations by Porter*. He showed that the viscosity of a liquid is in all cases given by an equation of the form $f(\eta) = A_2 + \frac{B_2}{T}$, where $f(\eta)$ is the same function of η for each substance, but whose form was not determined by the investigation, and A_2 and B_2 are constants which depend on the nature of the liquid. The writer found that a fair agreement with the facts is obtained on putting $f(\eta) = \eta^{\frac{1}{4}}$. Using this form of the function, the values of the constants A_2 and B_2 were determined from the viscosity of *n*-octane. Equation (27) then became

$$\eta = \frac{m^{\frac{5}{6}} p_c 10^{-14}}{T_c^{\frac{1}{2}} \rho_c^{\frac{1}{3}}} \left\{2{\cdot}29 + 3{\cdot}245 \frac{T_c}{T}\right\}^4 \quad \ldots\ldots\ldots\ldots(28).$$

This equation is quite general but it will give only a rough agreement with the facts in some cases, since k_7 is only approximately the same for all substances at corresponding states. However, it gives one some idea how the viscosity depends on the nature of the liquid.

The Partial Pressures exerted by the Molecules in a Mixture.

We have seen† that if n_1 denotes the number of molecules in a substance crossing a plane 1 cm.^{2} in area in one direction, the pressure they exert is equal to $n_1 1{\cdot}26 \times 10^{-20} \sqrt{T m_1}$. This applies whether the molecules occur in a pure substance or in a mixture. In the case of a gas we then have

$$n_1 1{\cdot}26 \times 10^{-20} \sqrt{T m_1} = p_1 = \frac{RT}{m_1 v_1} \quad \ldots\ldots\ldots\ldots(29),$$

where p_1 denotes the partial pressure of the molecules 1, and v_1 the volume in which one gram of molecules 1 occurs. In the case of a liquid this equation does not hold. But an equation can be found which holds in general.

Each molecule 1 crossing the plane in question gives rise on the average to a pressure $1{\cdot}26 \times 10^{-20} \sqrt{T m_1}$ dynes independent of the density and nature of the mixture‡. The number crossing is equal to the average velocity V_1, and we must therefore multiply

* *Phil. Mag.*, April 1912, pp. 458—462. † *Ibid.*, July 1912, pp. 101—118.
‡ *Loc. cit.*

the right-hand side of equation (29) by the factor $\frac{V_1}{V_{t1}}$, where V_{t1} denotes the velocity a molecule has in the gaseous state at the same temperature.

But the number of molecules crossing the cm.^{2} is also influenced by the actual volume per c.c. of the molecules 1 and the other molecules in the mixture. In the case of a pure substance whose molecules exert no attraction upon one another, we must write $(v-b)$ instead of v, according to an investigation by van der Waals, where b denotes four times the actual volume occupied by the molecules. This result can be used as foundation in dealing with pure substances or mixtures in which the molecules exert attraction upon one another. Suppose we are dealing with a mixture of molecules 1 and 2 in which the concentrations are respectively N_1 and N_2. Let W_{11} and W_{12} denote respectively the radii of the spheres of action of two molecules 1 and a molecule 1 and 2, which give rise to actual collision between the molecules. Let w_1 and w_2 denote respectively the actual radii of a molecule 1 and 2. If the molecules exert no attraction upon one another we would have to write $\left\{v_1 - N_1 4 \times \frac{4}{3}\pi w_1^3 - N_2 4 \times \frac{4}{3}\pi\left(\frac{w_1+w_2}{2}\right)^3\right\}$ instead of v_1. But the attraction between the molecules increases the chances of collision of a molecule 1 with a molecule 1 and a molecule 1 with a molecule 2 in the ratio $\frac{W_{11}}{w_1}$ and $\frac{W_{12}2}{w_1+w_2}$ respectively. We must therefore write

$$\left\{v_1 - N_1\frac{16}{3}\pi W_{11}w_1^2 - N_2\frac{16}{3}\pi W_{12}\left(\frac{w_1+w_2}{2}\right)^2\right\}$$

instead of v_1. Since $V_{t1} = \left(\frac{3RT}{m_1}\right)^{\frac{1}{2}}$ and $v_1 = \frac{1}{N_1 m_{a1}}$, where m_{a1} denotes the absolute mass of a molecule, equation (29) may now be written

$$n_1 = V_1\left(\frac{R}{3}\right)^{\frac{1}{2}} \frac{1{\cdot}27\times10^{-4}N_1}{\left\{1 - N_1^2 m_{a1}\frac{16}{3}\pi W_{11}w_1^2 - N_1N_2m_{a1}\frac{16}{3}\pi W_{12}\left(\frac{w_1+w_2}{2}\right)^2\right\}} \quad \ldots\ldots(30).$$

The equation corresponding to the molecules 2 is obtained by interchanging the suffixes 1 and 2 in the foregoing equation, where $W_{12} = W_{21}$. The equations are perfectly general.

The values of W_{11} and W_{12} we should expect to be proportional to the distance the two molecules must approach one another so as not to get separated again, in which case actual collision is certain to occur. The condition for this is that the kinetic energy of a

molecule must be proportional to the change in potential energy on approach of the molecules. Using the approximate expression for the attraction between two molecules, we then have in one case

$$T = \int_{\infty}^{W_{12}} \frac{K \Sigma \sqrt{m_1'} \Sigma \sqrt{m_2'}}{z^5} . dz.$$

Hence the values of the radii are approximately given by

$$W_{11} = X (\Sigma \sqrt{m_1'})^{\frac{1}{2}},$$

$$W_{12} = X (\Sigma \sqrt{m_1'} \Sigma \sqrt{m_2'})^{\frac{1}{4}},$$

$$W_{22} = X (\Sigma \sqrt{m_2'})^{\frac{1}{2}},$$

where X is a function of the temperature and nature of the mixture. The radius W of two molecules must be somewhat affected by the vicinity of other molecules; account of this is taken by giving an appropriate value to X.

According to Traube* the volume of a molecule at the absolute zero is proportional to $\Sigma \sqrt{m'}$, and we may therefore write

$$w_1 = k \Sigma \sqrt{m_1'},$$

$$w_2 = k \Sigma \sqrt{m_2'},$$

where k is a constant.

* *Phys. Zeit.*, Oct. 1909, p. 667.

PROCEEDINGS

OF THE

Cambridge Philosophical Society.

The Unit Theory of Light. By Professor Sir J. J. Thomson, O.M., F.R.S.

[*Read* 6 May 1912.]

On the unit theory of light, radiant energy is supposed to have a molecular structure and to be made up of a finite number of units. For light with a given periodicity, the energy in each unit is constant; the magnitude of the unit depends, however, upon the periodicity, and on Planck's theory is proportional to the frequency of the light. For light of frequency p the numerical value of the unit on this theory is $6{\cdot}55 \times 10^{-27}p$ ergs. This view of the structure of light has been introduced for the purpose of explaining the connection between the radiation from a black body and the temperature of the body; in this case when the light is emitted we have the transformation of thermal into radiant energy, and when light is absorbed the transformation of radiant into thermal energy. In every case in which this conception of the unitary character of light is helpful we are concerned, I think, with transformation of energy, while when we are dealing with purely optical phenomena, such as interference and the like, the same conception leads us into great difficulties, and in the present state of the subject at any rate is a hindrance and not a help.

A view that seems to me to be more in accordance with the facts is that though radiant energy may not be distributed continuously through the space through which the light passes, it is not as on the preceding view made up of constant and invariable units; the mechanism, however, by which the transformation of radiant energy into thermal energy or thermal energy into radiant is effected is a process which has an element of discontinuity in it, inasmuch as it proceeds by jumps and not continuously. The

transformation is supposed to be effected by the repetition of a process in which the amount of energy transformed is finite and definite, and consequently the total amount of energy transformed is always an integral multiple of a definite unit. Thus when transformations from thermal into radiant energy or from radiant into thermal are an essential part of the phenomenon, the effects produced will be the same as if the light itself were made up of definite units, while the explanation of purely optical effects where no transformations of energy are involved would practically be the same as on the old continuous theory. I discussed a view of this kind in some lectures I gave at the Royal Institution this spring and also in a paper in the *Philosophical Magazine* for May 1912. In this paper I wish to enter more fully into some questions raised by this theory.

Let us begin by considering the case of the absorption of light. Let us for the moment suppose that the light is monochromatic, to get absorption it is not sufficient to have in the absorbing medium systems in tune with the light passing through them. To take a simple illustration, suppose we had a frictionless perfectly elastic spring supporting a charged body, if this were acted on by electric waves of its own period it would absorb energy from the waves; after the waves had passed over it, however, the spring would go on vibrating for some time, losing its energy by the radiation of electric waves and it would not come to rest until all the energy given to it by the wave had been radiated away as electrical waves of the same period as the primary waves incident upon the spring. Thus the energy absorbed by the spring would be given out again later on as energy of the same type, this is merely a scattering of the primary wave, not absorption. To get real absorption of the light the energy that was in the light-wave must be transformed into a type of energy other than that of a system of charged bodies vibrating with the period of the incident light. In most cases when light is absorbed the energy in the light is transformed into heat, in others into the energy of chemical separation; in either case it is into a form from which the periodic character of the original energy has disappeared.

To go back to our original example, that of the spring. If this snapped when the charged body had acquired a certain amount of energy, the spring would act as a true absorber of energy, the energy absorbed being that required to break the spring. Thus with a system of springs of this kind the energy absorbed would always be a multiple of a definite unit, the amount of energy required to break the spring. If the energy given to a spring were less than this unit the spring would emit it later as energy of electrical vibrations of the same type as those from which it derived it and there would not be true absorption.

Let us consider another case where we might expect that light would be absorbed and not merely scattered by the substance through which it passed. Let us suppose that in the atoms of this substance there are systems of corpuscles with definite times of vibration and that some of these are in resonance with the monochromatic light which we are considering. Now the properties of gases, especially the values of their specific heats, show that up to the highest temperatures to which we can at present attain there is no approach to anything like equipartition of energy between the corpuscles and the molecules and atoms; the variation with temperature of the energy of each individual corpuscle is infinitesimal in comparison with that of the molecules, and the energy in the one does not, as it should according to the law of equipartition, keep getting transformed into or from that of the other until their average energies become equal or are in a constant proportion. In this case, when there is little or no transference of energy between the corpuscles and the atoms, if the corpuscles were set in motion by the electric forces in the light-wave, they would not communicate their energy to the molecules and thereby raise their temperature; the kinetic energy of the corpuscles would, after the wave had passed over, be dissipated as light-waves having the same period as the incident wave, and there would be scattering of the light but no absorption. Suppose now, however, that the system got so much energy that a corpuscle became detached and flew out of the system, then if w is the amount of energy required to detach the corpuscle from the system, w units of energy would disappear from the ranks of energy with the given periodicity and there would, for a time, be absorption of the energy in the light. If the corpuscle remained free for a time and then fell back again into the system it had left or a similar one which had also lost a corpuscle, it would, when it reached the system, have acquired w units of kinetic energy, the system would vibrate with the given period, and this energy would be dissipated as electrical waves with this period; taking the two processes, the detachment of the corpuscle and its return, together there would again be no true absorption, but merely a transference of w units of energy from the primary to the secondary wave.

Suppose, however, that after the corpuscle is ejected it gets attached to a molecule or an atom or some system of much greater mass than itself, then when it is attracted back to the system it has left or to a similar system which has also lost a corpuscle, it will drag the heavy mass along with it, and give to this mass kinetic energy, this kinetic energy, being that of an atom or molecule, will appear as heat energy, while the corpuscle itself when it regains the system will be moving so slowly as

hardly to start vibrations in the system. We may remark in passing that it is by a process of this kind that the transformation of the energy of Röntgen radiation into heat when the rays are absorbed by gas is effected. The rays ionise the gas detaching a corpuscle from some of the atoms, this corpuscle sticks to an atom or molecule, giving it a negative charge, and the attraction between this and the positively electrified residues sets both these into motion, and as the moving bodies are atoms or molecules their kinetic energy appears as heat.

To return to the case of light, we see that by a process of this kind the energy of the light would be transformed into heat energy and there would be a true absorption of the light. We see, too, that the amount of energy so transformed is a multiple of the unit w, while if, as in my paper in the *Philosophical Magazine*, we suppose that the return of an unattached corpuscle to its system is the cause of the radiation, we see that the light-energy is emitted in units each equal to w.

In the case of infra-red radiation such as *rest-strahlen* and the long waves recently investigated by Rubens, where the moving electrified bodies are more probably atoms or radicles than corpuscles, the absorption and emission might be continuous and not by multiples of a definite unit. Consider for example the case of a diatomic molecule AB. Part of its energy is due to the motion of the centre of gravity of A and B, part to the rotation of A and B round each other. Now in this case the value of the ratio of the specific heats shows that the energy due to the translation bears a constant ratio to that due to the rotation, so that any increase in the energy of rotation will be accompanied by an increase in the energy of translation and therefore by an increase in the temperature. Now if A and B are rotating round each other in a definite period and are exposed to the action of light of the same period, they will absorb energy from the light, and this energy will by the ordinary collisions between the molecules be transformed, partly at any rate, into heat energy. In this case there would be nothing corresponding to the detachment of a corpuscle from the system; there would be no natural unit of energy and the absorption of energy might be continuous. The absorption of the infra-red radiations by various gases such as ammonia and water vapour, the measurements of which by Rubens have recently yielded such interesting results may possibly be of this character. It would probably, however, be difficult to distinguish in the case of these very long waves between the theory of continuous absorption and absorption of a unitary character, unless the experiments were made at very low temperatures; for on the unitary theory the unit gets smaller and smaller as the wave-length increases, so that the effects on the

unitary theory approximate more and more closely to those on the continuous theory.

If we make the assumption that the absorption of the energy in the light involves the detachment from a system of a corpuscle with an expenditure of w units of energy we can calculate the rate at which the energy of light of a given period is absorbed by a number of such systems.

Consider the case of a spring with one degree of freedom which breaks when it has absorbed w units of energy and suppose that it is acted on by a periodic force in resonance with it. To make the case more analogous to that of light we shall suppose that the force acts for a certain time and then stops and after an interval begins again and that the phase of the force when it recommences is in no way related to the phase in the first period. The problem is to find the average energy communicated to a vibrating body by n successive applications of a force in tune with the body, the phases of the n successive applications of the force being quite arbitrary. When an electric force represented by $X \cos pt$ acts on a mass m attached to a spring and charged with e units of electricity then if its free vibrations have the frequency p, the equation of motion is

$$m\frac{d^2x}{dt^2} + \mu x = Xe \cos pt$$

where

$$p^2 = \mu/m.$$

The solution of this equation is

$$x = \frac{1}{2}\frac{Xet}{mp} \sin pt + \text{purely periodic terms}$$

or

$$\frac{dx}{dt} = \frac{1}{2}\frac{Xe}{m} . t \cos pt + \text{periodic terms.}$$

Taking account only of the first term we see that the force $Xe \cos pt$, acting for a time t, supposed large compared with $1/p$, increases the velocity by

$$\frac{1}{2}\frac{Xe}{m} t \cos pt.$$

Hence by the theory of the composition of vectors of arbitrary phase (see Lord Rayleigh, *Theory of Sound*, Vol. I. p. 40), when n forces $Xe \cos pt$, $Xe \cos (pt + t_1)$, $Xe \cos (pt + t_2)$ act in succession on the spring; t_1, t_2, etc. being arbitrary the most probable value of $\left(\frac{dx}{dt}\right)^2$ when the number n is large is

$$\frac{1}{8}\frac{X^2e^2}{m^2} t^2 \times n.$$

This expression is got on the supposition that the time t during which the force acts is the same in each case. If w is the kinetic energy of the bob necessary to break the spring, then n the average number of applications of the force required to break the spring is given by the equation

$$n = \frac{16w}{\frac{X^2e^2}{m}t^2}.$$

If the intervals between the various forces are small compared with t, the duration of each spell of force, nt will be the average time taken to break the spring, and w/nt will be the average rate at which energy is absorbed by the system, and this by the preceding equation is equal to

$$\frac{X^2e^2}{m} \cdot \frac{t}{16}.$$

If there are n such systems in unit volume absorbing energy the average rate at which energy is absorbed is

$$\Sigma\, n\delta v \frac{X^2e^2}{m} \cdot \frac{t}{16}$$

where δv is the volume through which the electric force is equal to X. But if E is the energy per unit volume due to the light, then

$$E = \Sigma \frac{\delta v \,.\, X^2}{4\pi \,.\, c^2}$$

where c is the velocity of light through the medium. Thus the rate at which energy is absorbed per unit volume is

$$\frac{n\pi}{4}\frac{e^2c^2}{m}t \cdot E.$$

It is possible that some of this energy may appear again as electric waves, as some of the corpuscles liberated by the light may fall back while still in the corpuscular state and give out the energy again in this form, and these ought not to be counted as producing absorption. Suppose that this return of the corpuscle occurs in a fraction k of the cases in which a corpuscle is split off, then A the absorption of light-energy per second per cubic centimetre is given by the equation

$$A = \frac{\pi}{4}\frac{nc^2e^2t}{m} \cdot E(1-k).$$

Let us now turn to the case of the production of the radiation. We shall make the same supposition as in the paper in the *Philosophical Magazine*, May 1912, that the emission of the radiation

of this definite period is due to a corpuscle falling back into a system from which it had been detached or into a similar one. Owing to the attraction between the corpuscle and the system the corpuscle when it regains the system will have an amount w of kinetic energy, and this will diffuse away as radiant energy, the period of vibration being that of the system completed by the return of the corpuscle.

If ξ is the number of free corpuscles per unit volume, η the number of atoms which have lost a corpuscle, then the number of recombinations in which the corpuscle is restored to its own or to a similar system is proportional to $\xi\eta$ and the energy radiated to $w\xi\eta$. Now consider equilibrium between the three phases measured by ξ, η, and n, n being the number of the undissociated systems. It requires an expenditure of energy equal to w to pass from the phase n to the phase $(\xi\eta)$. Hence by the Theory of Dissociation (see J. J. Thomson, *Application of Dynamics to Physics and Chemistry*, p. 199),

$$\xi\eta = nf(\theta)\,\epsilon^{-\frac{w}{R\theta}}$$

when θ is the absolute temperature of the system, R the gas constant and $f(\theta)$ a function of θ only. Since the rate at which radiation is emitted per unit volume is proportional to $\xi\eta$ it will by the preceding equation be proportional to

$$wnf(\theta)\,\epsilon^{-\frac{w}{R\theta}},$$

hence if the energy emitted is equal to the energy absorbed, as it will be when things are in a steady state, we have

$$wnf(\theta)\,\epsilon^{-\frac{w}{R\theta}} = \alpha\frac{\pi}{4}nE\frac{e^2c^2}{m}b\,.(1-k)$$

when α is a constant, or

$$E = \frac{4wm\alpha}{\pi e^2c^2t}\frac{f(\theta)\,\epsilon^{-\frac{w}{R\theta}}}{1-k}.$$

The period of vibration of the light does not appear explicitly in this expression for E, the quantity which takes its place is w the work required to separate a corpuscle from the system. This work will, however, be connected with the time of vibration and for systems of a certain type w will be proportional to the frequency of the vibrations. For suppose the system from which the corpuscle is withdrawn consists of an electrical doublet AB and the corpuscle P; the corpuscle being prevented falling into the doublet by a strong magnetic field, the lines of magnetic force being at right angles to $AB.P$: then if M is the electrical

moment of the doublet, the frequency of the vibration of a corpuscle displaced at right angles to AB

$$= \sqrt{\frac{2Me}{m \cdot OP^4}}.$$

The work required to remove the corpuscle from the system

$$= \int_{OP}^{\infty} \frac{2Me}{r^2} dr = \frac{Me}{OP^2},$$

hence if p is the frequency,

$$p = w \sqrt{\frac{2}{Mme}},$$

so that in this case w is proportional to p and the exponential term in the expression for E will take the form $\epsilon^{-\frac{\beta p}{R\theta}}$, as in Planck's expression.

It may be objected that inasmuch as on our view the radiation is due to the falling in of a corpuscle and that by this process a finite and definite amount of energy is radiated from the system, light on this view is made up of finite units just as on Planck's theory; this objection is, however, founded on a misconception. It is true that on this view the light is emitted with a definite amount of energy, but this energy only remains intact as long as the light does not pass through matter. When it passes through matter it sets systems of corpuscles in vibration, and these vibrations give rise to scattered light whose energy is derived from that in the primary, so that when light has passed through any considerable portion of matter the energy in the primary bundle will have been divided up into a great number of portions with probably no kind of equality between them. This subdivision of the light up into these much smaller subdivisions makes the structure in a light-wave much more nearly continuous than on Planck's theory, and this close approach to a continuous distribution avoids all the difficulties about the interference of very faint light which are so formidable on that theory. The greater the number of atoms passed over by the primary wave the greater is the subdivision of its energy and the more closely does the distribution of energy in the radiation approach to the continuous distribution postulated on the ordinary theory of light. If the light were produced in gas at a very low pressure we should expect that in the gas itself the energy in the radiation emitted by a luminous atom or molecule would not be nearly so much subdivided as after it had passed through the glass walls of the tube enclosing the gas, and so that the energy in the light inside the vacuum tube might be not nearly so uniformly distributed

through space as when it got out of the tube. It would be interesting to test this point by seeing whether interference fringes could be produced as easily and to the same extent in a good vacuum as under ordinary conditions: the light being produced in the vacuum either by the electric discharge, or preferably by canal rays.

The rapidity with which the energy in the primary beam would be subdivided up into secondary beams would also depend to a considerable extent upon the number of wave-lengths included in the train of primary radiation. If there are only a few wave-lengths in this train resonance will hardly have time to come into play and there would not be much loss of the primary energy in the formation of secondary waves. There will only be a few waves in the primary beam when it comes from the luminous atom if the dissipation of the kinetic energy of a system of corpuscles by radiation is very rapid, so rapid that all the energy is exhausted before more than a small number of vibrations have taken place, we might expect that this would occur with very small wave-lengths, such as those comparable in thickness with a Röntgen pulse. If radiation of this kind were shot out from the vibrator in a definite direction and not uniformly over the whole of the surface of a sphere, it would continue to travel along this direction, losing but slowly either definiteness of outline or energy; in such cases as these resonance would be of but little importance, the energy communicated to a system in the path depending mainly on the energy in the primary beam. Thus in the case of the emission of negative corpuscles from a piece of metal exposed to Röntgen rays a corpuscle may be able to get its energy from a single pulse of Röntgen radiation. When, however, corpuscles are emitted from the metal under the action of ordinary light, the energy in the radiation has probably undergone considerable subdivision since it was emitted from the luminous molecule, and we should expect resonance to come into play. I have suggested that the fact that the velocity of the corpuscles ejected, while they depend on the wave-length of the incident light, is to a considerable extent independent of the intensity, can be explained by the existence within the molecules of corpuscles describing orbits round electrical doublets with a velocity proportional to the square root of their frequency round their orbits. Light of this frequency acts by resonance on the doublets, twisting them round until they can no longer retain the corpuscles which escape with a velocity which is thus fixed by the frequency of the light-vibration.

As these corpuscles possess a definite amount of energy e when they are emitted they will be able to detach a corpuscle from a system with which they come into collision if the energy e_1

required for this purpose is less than e. The falling back of this corpuscle into the system from which it was detached will cause a wave-train of energy e_1 (e_1 less than e) to be emitted from the system, and as the energy is proportional to the frequency the frequency of the light excited in this way, "the fluorescent light," will be less than that of the incident light. Similar considerations apply to the characteristic Röntgen radiation which is emitted by the elements when they are exposed to Röntgen rays harder than the characteristic. This characteristic radiation may be regarded as due to the return of a corpuscle to a system from which it has been detached. When the hard radiation falls on the element it gives rise to the emission of corpuscles which have so much energy that they are able to detach corpuscles from the systems responsible for the characteristic radiation; they only do so, however, because the characteristic radiation is softer than the incident. If the incident were softer than the characteristic, the corpuscles shot out by the incident light would not have sufficient energy to dissociate the system producing the characteristic radiation.

On the Mobility of the Negative Ion at Low Pressures. By George W. Todd, M.Sc., B.A.; 1851 Exhibition Scholar of Birmingham University; Emmanuel College, Cambridge. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 29 July 1912.]

From the experiments of Langevin and Kovarik it is generally assumed that at low pressures the negative ions in gases have greater mobilities than the inverse pressure law requires. The experimental evidence however has been confined to two gases only—air and carbon-dioxide. In some work by the writer on the mobilities of positive ions at low pressures* it has been found that these also depart from the law but at a much lower pressure than in the case of the negative ions. For different gases this critical pressure appears to be approximately proportional to the mobility of the ion in the gas at ordinary pressures so that the denser the gas the lower the pressure is at which the abnormal increase in the mobility begins. In some work not yet published the author finds that this relation between the critical pressures holds good but the critical pressure itself depends on the dimensions of the apparatus and the magnitude of the alternating electric field.

The present paper contains the results of some experiments on the variation of the mobility with the pressure for the negative ions in several gases; and for the same apparatus and if the rate of alternation of the field is kept constant, a similar relation is found to hold between the critical pressure and the normal mobility as holds for the positive ion.

As the apparatus used was almost identical with that described in a previous communication to this society† there will be no need to describe its detail. A section of the gas in a vessel at reduced pressure was ionised by a beam of Röntgen rays and the negative ions produced were directed to a gauze beyond which there was an alternating electric field, uniform at every instant. The field which directed the negative ions to the gauze of course conducted the positive ones away from the alternating chamber. A metal plate in connection with a tilted electroscope formed one boundary of the alternating chamber while the gauze formed the other. By gradually increasing the intensity of the alternating field a point would be reached when the electroscope plate began to receive a charge. From this value of the field the mobility was calculated.

* *Phil. Mag.*, Nov. 1911, p. 791.
† *Proc. Camb. Phil. Soc.*, xvi. 21.

The following tables and curves show the relation between the pressure and the product of pressure and mobility for the gases on which experiments were made.

Air

Pressure (cms.)	15·1	13·6	9·8	7·35	5·72	4·38	3·61
pk	156	157	160	179	218	262	332

CO_2

Pressure (cms.)	12·3	7·72	5·38	4·39	3·81	3·11	2·80	2·23	1·91
pk	84	90	97	113	112	130	170	204	219

H_2S

Pressure (cms.)	15·3	11·6	6·72	5·20	4·33	3·61	2·92	2·42	1·87
pk	60	59	62	66	69	71	81	91	95

SO_2

Pressure (cms.)	10·4	5·92	3·63	2·48	1·77	1·26	·98
pk	39	41	37	43	41	46	41

H_2

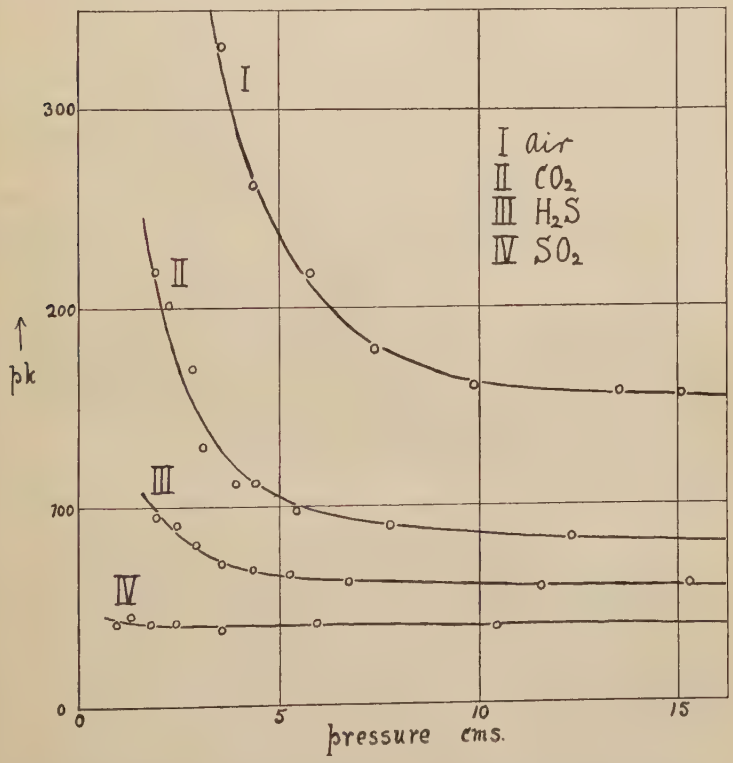
Pressure (cms.)	28·0	22·9	17·1	13·3
pk	630	730	750	890

It will be observed that roughly the pressures at which the mobilities begin to show abnormality are proportional to the normal mobilities in the gases. With air and carbon-dioxide the abnormal increase begins at a lower pressure than that observed by Langevin and Kovarik, both of whom used those two gases. An explanation of this difference is probably to be sought for in the fact that in these investigators' experiments the ions were produced *inside* the measuring chamber while in the present experiments they were formed *outside* and had time to reach an equilibrium condition before being subjected to the alternating field. Kovarik* found that at low pressures the rate of alternation of the field made a difference in the mobility of the ions and the lower the pressure the bigger was this difference. This fact agrees with the explanation that the ions require an appreciable time to reach an equilibrium state. For with a higher rate of alternation, a higher maximum potential would be required to take the ions across the measuring chamber, and if the ions in their initial stage were corpuscles they would travel a bigger fraction of the distance in a large field than in a small one, before reaching equilibrium conditions.

There is evidence that even after traversing several hundreds of free paths many ions exist in their initial simple condition.

* *Phys. Rev.*, xxx. 4, 420.

Dempster*, who has measured mobilities of positive and negative ions at very high pressures, mentions some results with the negative ions which support this view. He produced his ions in an ante-chamber and introduced them into the alternating chamber by putting on a field, much in the same way as in the writer's experiments. Although there must have been many hundreds of collisions he observed that an intense driving field in the ante-chamber resulted in bigger mobilities. Townsend† has pointed out that a considerable number of ions exist as corpuscles at a distance of 8000 free paths from their birthplace, and this when the field was much too small to cause ionisation by collision.



It is reasonable to suppose that however low the pressure, given sufficient time, the ion would reach an equilibrium state identical with that at high pressures. Some experiments were made, not very successful but perhaps interesting to mention, to test this

* *Phys. Rev.*, xxiv. 53.
† *Phil. Mag.*, 1912, 857.

point and to find how far the corpuscles must travel before reaching a steady state.

The ions in this case—one could not get sufficient at the lowest pressures with X-rays—were produced by heating lime to incandescence on a strip of platinum. By means of a wire wound on a glass rod projecting through a ground glass joint into the containing vessel, the distance of the strip of platinum from the gauze of the alternating chamber could be adjusted. To allow for their necessary movement up and down the leads to the strip dipped into long glass tubes containing mercury.

On making experiments with the hot strip within one or two millimetres of the gauze the mobilities were found to vary considerably with the temperature of the strip, while at distances of one or two centimetres temperature made no difference to the mobility obtained. This increase in mobility with increase in temperature of the strip when the source of ions was near the gauze of the alternating chamber shows that apart from distance temperature has a big effect on the mobility. Varying the distance of the strip at close quarters, keeping it at constant temperature, gave different mobilities due to the penetration to different distances of the sphere of heated gas round the platinum into the measuring chamber, and also to the effect sought for if it existed. There was no way of separating the effects easily.

When the distance and temperature of the strip, and the pressure of the gas were maintained constant so that the heating effects would be constant, it was found that increasing the "driving" potential increased the mobility. This was much more evident with the strip at a millimetre than at a centimetre from the gauze. It was also less evident at a higher pressure than at a lower pressure, as might be expected. This will be seen from some of the readings given below.

Pressure = 8·6 cms.		Distance of strip = 3·1 cms.			
Driving potential	12	20	30	40	80
Mobility	169	170	170	176	180

Pressure = 8·6 cms.		Distance of strip = 0·2 cm.			
Driving potential	12	20	30	40	80
Mobility	191	196	199	210	232

Pressure = 3·2 cms.		Distance of strip = 3·2 cms.			
Driving potential	12	20	30	40	80
Mobility	339	338	348	350	359

Pressure = 3·2 cms.		Distance of strip = 0·1 cm.			
Driving potential	12	20	30	40	80
Mobility	409	419	431	448	469

The increased mobilities at the same pressure with the strip at the shorter distance must be put down to the increase in temperature of the measuring chamber.

At these pressures the ions must experience many hundreds of collisions before reaching the gauze of the alternating chamber and even then they cannot have reached equilibrium as the effect of variation in the driving force shows. When the source of ions was at a big distance from the gauze so that there would be no heating effect in the alternating chamber the mobilities at the lowest pressures even with the smallest driving fields were above the normal value. In some experiments, the results of which are not yet published, the author has been able to get positive ions to oscillate under an alternating field over a distance of more than 20 cms. With the same apparatus a few experiments were made with negative ions from a lime-covered strip of platinum and it was found that with the "alternating" distance ten times as great as that used in the experiments described in this paper and using fields of one-tenth the magnitude, the mobilities at low pressures approached nearer the normal value. It appears that the violence of collision due to too big fields prevents the formation of the cluster of which the normal ion consists. With weaker fields and greater distances the mobilities at low pressures fall nearer the normal value.

The author expresses his thanks to Sir J. J. Thomson for his kind interest in these experiments.

On the Exact Form of the Law of Molecular Attraction. By R. D. KLEEMAN, B.A., Emmanuel College, D.Sc. (Adelaide).

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In a number of previous papers* the writer has investigated the law of the molecular attraction which gives rise to the surface tension and the internal heat of evaporation of liquids. It was shown that the attraction between two molecules of the same kind at the temperature T and separated by the distance z, is given by

$$\phi\left(\frac{T}{T_c}, \frac{x_c}{z}\right) \cdot \frac{(\Sigma\sqrt{m_1'})^2}{z^5},$$

which we will write for shortness

$$(\phi) \cdot \frac{(\Sigma\sqrt{m_1'})^2}{z^5},$$

where x_c denotes the distance of separation of the molecules in a quantity of liquid at the critical state and temperature T_c, and $\Sigma\sqrt{m_1'}$ denotes the sum of the square roots of the atomic weights of the atoms of a molecule. It was further shown that the exact form of the function (ϕ) cannot be determined from surface tension or latent heat data. Investigations† of the form of the function in connection with the diffusion of gases, the Joule-Thomson effect, etc., show that as a rough approximation it may be taken to be a function of the temperature only and written $\frac{K}{T}$, where K is a constant. In this paper the exact form of the function will be investigated more fully than has been done in previous papers.

Since the function may be taken approximately as a function of the temperature only, we may suppose that one of the terms it contains is B, where B is a function of $\frac{T}{T_c}$, which gives rise to the term $\frac{B}{z^5}(\Sigma\sqrt{m_1'})^2$ in the law of molecular attraction. Experiments on the Joule-Thomson effect have shown that the attraction between two molecules changes to repulsion when they are separated by a sufficiently large distance. The function (ϕ), or the law of molecular attraction, thus consists of a number of positive

* *Phil. Mag.* Jan. 1911, p. 97; and previous papers.

† *Ibid.*, May 1910, p. 806; *Proc. Camb. Phil. Soc.* Vol. XVI. Pt VI. p. 555, and Pt VII. pp. 588—591.

and negative terms*. The principal negative term in the law of molecular attraction which gives rise to this repulsion must contain an inverse power of the distance of separation of the molecules which is less than the fifth, since its importance in comparison with the foregoing term must increase with the distance of separation of the molecules. We shall assume this power to be the fourth, since there is nothing to indicate its exact magnitude. This term may therefore be written $\frac{A}{x_c z^4}(\Sigma\sqrt{m_1'})^2$, where A is a function of $\frac{T}{T_c}$. In a previous paper† evidence was obtained that the attraction between two molecules changes to repulsion for distances of separation of the order of the diameter of a molecule. The law of molecular attraction must therefore contain a term consisting of an inverse power of z which is greater than the fifth. Since there is nothing to indicate its magnitude, we will assume that it is the sixth; and this term may accordingly be written $\frac{Cx_c}{z^6}(\Sigma\sqrt{m_1'})^2$, where C is a function of $\frac{T}{T_c}$. We shall accordingly assume that the attraction between two molecules is approximately given by the expression

$$\left\{A\frac{z}{x_c}+B+C\frac{x_c}{z}\right\}\frac{(\Sigma\sqrt{m_1'})^2}{z^5} \quad \text{.....(1).}$$

If the law of attraction of the molecules of a substance is given, we can at once calculate the intrinsic pressure P_n in the substance by means of a formula given by the writer‡. The above law of attraction gives

$$P_n=\left\{\frac{A2{\cdot}75}{x_c z^6}+\frac{B2{\cdot}06}{z^7}+\frac{C1{\cdot}63x_c}{z^8}\right\}(\Sigma\sqrt{m_1'})^2\text{.....(2),}$$

where $z=\left(\frac{m}{\rho}\right)^{\frac{1}{3}}$, $x_c=\left(\frac{m}{\rho_c}\right)^{\frac{1}{3}}$, ρ denotes the density of the substance at the temperature T and ρ_c that at the critical temperature, and m denotes the absolute mass of a molecule. The energy W expended per gram of substance against the molecular attraction on separating the molecules of a mass of substance by an infinite distance from one another, is connected§ with the intrinsic pressure by the equation

$$\frac{dW}{dv}=\frac{m\,.\,dW}{d(z^3)}=\frac{m}{3z^2}\cdot\frac{dW}{dz}=P_n,$$

* *Proc. Camb. Phil. Soc.* Vol. XVI. Pt VI. p. 556.
† *Ibid.* Vol. XVI. Pt VII. p. 584.
‡ *Phil. Mag.* Oct. 1910, pp. 666, 667.
§ *Proc. Camb. Phil. Soc.* Vol. XVI. Pt VI. p. 543.

where v denotes the volume of a gram of substance. Hence we have

$$W = \left\{ \frac{A1{\cdot}65}{x_c z^3} + \frac{B1{\cdot}03}{z^4} + \frac{C{\cdot}7x_c}{z^5} \right\} \frac{(\Sigma \sqrt{m_1'})^2}{m} \quad \ldots\ldots\ldots(3),$$

where z, x_c, and m have the same meaning as in the expression for P_n.

The values of A, B, and C at the critical point can be determined by the help of the equation of state. The equation may be written in the general form

$$p + P_n = \psi_1(T, \rho) \quad \ldots\ldots\ldots(4),$$

where p denotes the external pressure of the substance, and $\psi_1(T, \rho)$ a function expressing the effect of the motion of translation of the molecules, which balances the sum of the external and intrinsic pressures. Since according to the law of molecular attraction $p = ap_c$, $P_n = bp_c$, where p_c denotes the critical pressure*, and a and b are quantities which have the same values for all substances at corresponding states, $\psi_1(T, \rho)$ must have the form

$$\psi_2\left(\frac{T}{T_c}, \frac{\rho}{\rho_c}\right) p_c, \text{ or } \psi_3\left(\frac{T}{T_c}, \frac{\rho}{\rho_c}\right) \frac{RT}{m} \rho,$$

since according to the law of molecular attraction $p_c = \frac{RT}{3{\cdot}7 m_1} \rho_c$†, where m_1 denotes the molecular weight relative to that of hydrogen. In the case of a perfect gas $\psi_3\left(\frac{T}{T_c}, \frac{\rho}{\rho_c}\right) = 1$. We may therefore in general write

$$\psi_3\left(\frac{T}{T_c}, \frac{\rho}{\rho_c}\right) = 1 + E\frac{\rho}{\rho_c} + F\frac{\rho^2}{\rho_c^2},$$

where E and F are functions of $\frac{T}{T_c}$. Equation (4) may now be written

$$p + \frac{A_1\rho^2}{\rho_c^{\frac{1}{3}}} + B_1\rho^{\frac{7}{3}} + C_1\frac{\rho^{\frac{8}{3}}}{\rho_c^{\frac{1}{3}}} = \frac{RT}{m_1}\rho\left(1 + E\frac{\rho}{\rho_c} + F\frac{\rho^2}{\rho_c^2}\right) \ldots(5),$$

where $$A_1 = \frac{A2{\cdot}75}{m^{\frac{7}{3}}}(\Sigma\sqrt{m_1'})^2, \quad B_1 = \frac{B2{\cdot}06}{m^{\frac{7}{3}}}(\Sigma\sqrt{m_1'})^2,$$

and $$C_1 = \frac{C1{\cdot}63}{m^{\frac{7}{3}}}(\Sigma\sqrt{m_1'})^2.$$

* *Phil. Mag.* March 1911, p. 337, and Oct. 1910, p. 668.
† *Ibid.* Dec. 1909, p. 905.

The values of the quantities A_1, B_1, C_1, E, and F can be determined by applying the critical point conditions to equation (5). These conditions are that

$$f=0,\ \frac{\delta f}{\delta v}=0 \text{ or } \frac{\delta f}{\delta \rho}=0,\ \frac{\delta^2 f}{\delta v^2}=0 \text{ or } \frac{\delta^2 f}{\delta \rho^2}=0,$$

$$\left[\frac{d}{dv}(W+w)\right]_T=-6{\cdot}5p_c,\ (W+w-w_a)\,\rho_c=6{\cdot}5p_c,$$

at the critical point, where $f=0$ denotes the equation of state. The quantity w denotes the internal energy of the molecules of a gram of substance in the critical state, and w_a its value when the molecules are in the gaseous state. We will assume that $w-w_a$ and $\frac{dw}{dv}$ are equal to zero. We also have

$$\frac{dW}{dv}=P_n \text{ or } W=\int_0^{\rho}-\frac{P_n}{\rho^2}.d\rho.$$

The first three conditions follow from the continuity of state, and are those usually given. The remaining two conditions have been given by the writer*. On applying these conditions to equation (5) we obtain that $A_{1c}=-16p_cv_c^{\frac{7}{3}}$, $B_{1c}=60p_cv_c^{\frac{7}{3}}$, $C_{1c}=-37{\cdot}5p_cv_c^{\frac{7}{3}}$, $F_c=-6$, and $E_c=12{\cdot}5$. Hence we deduce that

$$A_c=-{\cdot}439\times10^{-44},\ B_c=2{\cdot}2\times10^{-44},\text{ and } C_c=-1{\cdot}74\times10^{-44},$$

using the values of p_c, v_c, $\Sigma\sqrt{m_1'}$, and m, of ether, and for the absolute mass of the hydrogen atom the value $1{\cdot}61\times10^{-24}$ grm. deduced by Rutherford from experiments on the α particle. It will be noticed that the signs of the quantities A_c, B_c, and C_c, are as anticipated.

The attraction between two molecules at the critical temperature separated by the distance z is therefore

$$\left\{-\frac{z{\cdot}439}{x_c}+2{\cdot}2-\frac{x_c}{z}1{\cdot}74\right\}\frac{(\Sigma\sqrt{m_1'})^2}{z^5}10^{-44}\text{ dyne.}$$

It is interesting to compare this expression with that obtained in a different way on the supposition that (ϕ) is a function of the temperature only. The latter expression is $2{\cdot}97\times10^{-45}\frac{(\Sigma\sqrt{m_1'})^2}{z^5}$, corresponding to a temperature of $\frac{2T_c}{3}$, obtained by means of data relating to ether†.

* *Phil. Mag.* Sept. 1912.
† *Proc. Camb. Phil. Soc.* Vol. XVI. Pt VII. p. 595.

On equating the former expression for the attraction to zero we obtain the distance of separation of the molecules at which the force between them changes sign. Thus we obtain

$$z = 2{\cdot}5x_c \pm 1{\cdot}522x_c = 4{\cdot}02x_c \text{ or } {\cdot}978x_c.$$

One of these distances is of the same order as the distance of separation of the molecules at the critical state, and the other is about four times this distance. In a previous part of the paper evidence was quoted that two molecules repel each other when they are separated by a distance of the same order as the diameter of a molecule, or that of the distance of separation of the molecules in the liquid state. This fits in with the result just obtained.

It will be of interest next to obtain expressions for A, B, and C, in terms of $\frac{T}{T_c}$. We have seen that the experiments on the Joule-Thomson effect indicate that the attraction between two molecules varies inversely as the temperature. But this can obviously apply over a certain region only; at the absolute zero, for example, it could not apply since it would make the attraction infinitely great. We will therefore suppose that each of the quantities A, B, and C, consists of an expression of the form $\frac{a}{r + T/T_c}$, where a and r are constants. We will also suppose, for convenience of calculation, that the temperature variation of each of the quantities indicating repulsion is the same. Accordingly we have $A = \frac{a}{r_1 + T/T_c}$, $B = \frac{b}{r_2 + T/T_c}$, and $C = \frac{c}{r_1 + T/T_c}$. At the critical point we then have

$$\frac{a}{r_1+1} = -{\cdot}439 \times 10^{-44}, \quad \frac{b}{r_2+1} = 2{\cdot}2 \times 10^{-44},$$

and $\frac{c}{r_1+1} = -1{\cdot}74 \times 10^{-44}$, and thus $a = c{\cdot}2523$. Additional equations involving the quantities a, b, c, r_1, and r_2 are obtained on applying equations (2) and (3) to a substance at a temperature below the critical temperature. Thus in the case of ether at the temperature 13·5° we then have

$$P_n = \left\{\left(\frac{2{\cdot}75 \times {\cdot}2523}{x_c z^6} + \frac{1{\cdot}63}{z^8}\right)\frac{c}{r_1 + T/T_c} + \frac{b2{\cdot}06}{z^7(r_2 + T/T_c)}\right\}(\Sigma\sqrt{m_1'})^2 \quad \text{.....(6),}$$

and

$$W = \left\{\left(\frac{1{\cdot}65 \times {\cdot}2523}{x_c z^3} + \frac{{\cdot}7x_c}{z^5}\right)\frac{c}{r_1 + T/T_c} + \frac{b1{\cdot}03}{z^4(r_2 + T/T_c)}\right\}\frac{(\Sigma\sqrt{m_1'})^2}{m} \quad \text{.....(7),}$$

where*

$$P_n = 2{\cdot}669 \times 10^9 \text{ dynes}, \quad W = 82{\cdot}58 \times 4{\cdot}2 \times 10^7 \text{ ergs}, \quad \frac{T}{T_c} = {\cdot}6128,$$

$$x_c = \left(\frac{m}{\rho_c}\right)^{\frac{1}{3}} = \left(\frac{74 \times 1{\cdot}61 \times 10^{-24}}{{\cdot}2604}\right)^{\frac{1}{3}}, \quad z = \left(\frac{m}{\rho}\right)^{\frac{1}{3}} = \left(\frac{74 \times 1{\cdot}61 \times 10^{-24}}{{\cdot}2604}\right)^{\frac{1}{3}},$$

and $(\Sigma\sqrt{m_1'}) = 27{\cdot}84$. From these equations we deduce that

$$a = -1{\cdot}042 \times 10^{-44}, \quad b = 2{\cdot}741 \times 10^{-44}, \quad c = -4{\cdot}131 \times 10^{-44},$$

$$r_1 = 1{\cdot}375, \text{ and } r_2 = {\cdot}2461.$$

Hence the expression for the molecular attraction becomes

$$\left\{-\frac{1{\cdot}042}{1{\cdot}375 + T/T_c}\frac{z}{x_c} + \frac{2{\cdot}741}{{\cdot}2461 + T/T_c} - \frac{4{\cdot}131}{1{\cdot}375 + T/T_c}\frac{x_c}{z}\right\}\frac{(\Sigma\sqrt{m_1'})10^{-44}}{z^5}$$

.....(8).

It will be seen that the molecular repulsion varies much less with the temperature than the attraction. The resultant attraction between two molecules will vary on account of the existence of repulsion more rapidly with the temperature than indicated by the factor $\frac{1}{{\cdot}2461 + T/T_c}$, and may therefore well vary approximately inversely as the temperature over a considerable range of temperatures, as indicated by the Joule-Thomson effect.

On equating this expression to zero when it corresponds to the absolute zero of temperature we obtain for z the values ${\cdot}27x_c$ and $14{\cdot}4x_c$. The force between two molecules changes sign at these distances of separation. On comparing them with the corresponding distances obtained for the critical temperature we see that the smaller distance decreased in magnitude while the larger distance increased. This shows that the higher the temperature above the critical temperature the smaller is the distance over which two molecules attract one another. Consequently on increasing the temperature of a gas a point is ultimately reached when the product pv always increases with p, and behaves in the same way for all higher temperatures. The gas has then a negative intrinsic pressure, or an intrinsic pressure of opposite sign as occurs in a liquid. This fits in with the shape of the isothermal curves connecting p and pv obtained for various gases at different temperatures, and with the experiments on the change of sign of the Joule-Thomson effect.

* *Proc. Camb. Phil. Soc.* Vol. xvi. Pt vi. p. 545.

Equations (2) and (3) now become

$$P_n = \left\{ -\frac{2{\cdot}865}{1{\cdot}375 + T/T_c}\frac{1}{x_c z^6} + \frac{5{\cdot}648}{{\cdot}2461 + T/T_c}\frac{1}{z^7} - \frac{6{\cdot}735}{1{\cdot}375 + T/T_c}\frac{x_c}{z^8} \right\} (\Sigma\sqrt{m_1'})^2 \quad \ldots\ldots\ldots(9),$$

$$\text{and } W = \left\{ -\frac{1{\cdot}719}{1{\cdot}375 + T/T_c}\frac{1}{x_c z^3} + \frac{2{\cdot}823}{{\cdot}2461 + T/T_c}\frac{1}{z^4} - \frac{2{\cdot}895}{1{\cdot}375 + T/T_c}\frac{x_c}{z^5} \right\} \frac{(\Sigma\sqrt{m_1'})^2}{m} \quad \ldots\ldots\ldots(10).$$

The Joule-Thomson effect changes sign when z has the values given by the equation $\left(\frac{dW}{dz}\right)_T = 0$, that is

$$-\frac{5{\cdot}157}{1{\cdot}375 + T/T_c} z^2 + \frac{11{\cdot}292 x_c}{{\cdot}2461 + T/T_c} z - \frac{14{\cdot}475}{1{\cdot}375 + T/T_c} x_c^2 = 0 \quad \ldots(11).$$

According to this equation there are two values of z, or two volumes of the substance, corresponding to each temperature, at which no heating or cooling is produced on changing the volume by δv. At the critical temperature, for example, z has the values ${\cdot}541 x_c$ and $3{\cdot}631 x_c$. Since the critical volume of a gram of substance is proportional to x_c^3, the Joule-Thomson effect will change in sign when the volume of the substance is ${\cdot}158 v_c$ and $47{\cdot}9 v_c$.

It follows also from equation (11) that the difference between the values of z, satisfying the equation, increases with decrease of temperature. The temperature at which the equation gives equal values for z is therefore a characteristic temperature of the gas. There is no inversion of the Joule-Thomson effect for higher temperatures, whatever the volume of the gas. This temperature is given by the equation

$$\frac{11{\cdot}292}{2 \times 5{\cdot}157}\frac{1{\cdot}375 + T/T_c}{{\cdot}2461 + T/T_c} = \left(\frac{14{\cdot}47}{1{\cdot}375}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots(12),$$

which expresses the condition for equal roots; and thus $T = 2T_c$ approximately. If the Joule-Thomson effect of a gas whose initial temperature is much greater than the critical temperature is measured progressively for lower temperatures, a temperature is ultimately reached when inversion of the effect takes place. In practice it is found to be of the order $3T_c$. It is thus of the same order as that given by equation (12).

The constants in the expression $\psi_1(T, \rho)$ can be determined

by the help of the equations obtained by applying equation (4) to a substance at different temperatures. It is necessary first, however, to make some supposition about the form of the temperature functions E and F. Let us assume that

$$E = A_1 + B_1 \frac{T}{T_c}, \text{ and } F = A_2 + B_2 \frac{T}{T_c}.$$

At the critical point we then have $A_1 + B_1 = 12{\cdot}5$ and $A_2 + B_2 = -6$. Let us apply equation (4) to ether at the absolute temperatures 273 and 373. The external pressure p may then be neglected in comparison with the intrinsic pressure P_n. The latter quantity may be taken* to be equal to $\frac{T\alpha}{\beta}$, where α denotes the coefficient of expansion with rise of temperature, and β the coefficient of compression at constant temperature. In the former case we have $P_n = 2669$ atmos., $\rho = {\cdot}7362$, and in the latter $P_n = 1375$ atmos., $\rho = {\cdot}6105$. We accordingly deduce $A_1 = 22{\cdot}57$, $B_1 = -10{\cdot}07$, $A_2 = 5{\cdot}01$, and $B_2 = -11{\cdot}01$. Hence equation (4) becomes

$$p + P_n = \frac{RT\rho}{m_1}\left\{1 + \left(22{\cdot}57 - 10{\cdot}07\,\frac{T}{T_c}\right)\frac{\rho}{\rho_c} + \left(5{\cdot}01 - 11{\cdot}01\,\frac{T}{T_c}\right)\frac{\rho^2}{\rho_c{}^2}\right\} \quad \ldots\ldots\ldots(13).$$

In a previous paper it was shown that

$$n1{\cdot}26 \times 10^{-20}\sqrt{Tm_1} = P_n + p,$$

where n denotes the number of molecules crossing a cm^2 in one direction per second. On combining this equation with the foregoing we obtain an equation expressing n in terms of T and ρ. The quantity n is of importance since it occurs in the general equations† giving the diffusion, viscosity, and conduction of heat of substances.

The Average Velocity of a Molecule in a Substance.

The principles applied in the foregoing section may be used to obtain an approximate expression for the average velocity of a molecule in a substance. It has been shown in previous papers‡ that the average velocity of a molecule in a liquid must be several times that which it has in the gaseous state at the same temperature. It was also shown that the average velocity of a molecule is the same multiple of its velocity as a gas molecule for all substances at corresponding states. Let us therefore assume that the average velocity is given by the expression $V_g\left(1 + a\,\frac{\rho}{\rho_c}\right)$, where V_g denotes

* *Proc. Camb. Phil. Soc.* Vol. xvi. Pt vi. pp. 543—546.
† *Phil. Mag.* July 1912, pp. 101—118.
‡ *Loc. cit.* p. 102; *Proc. Camb. Phil. Soc.* Vol. xvi. Pt vii. p. 594.

the velocity of the molecule in the gaseous state at the same temperature as the substance, and a is a constant. In previous papers* we have shown that $\psi_1(T, \rho)$ in equation (4) may be written $\frac{V_a}{V_g}\frac{RT}{m_1(v-b)}$, where V_a is the average velocity of a molecule, v the volume of a gram of substance, and b the space through which the centres of the molecules do not pass during their motion of translation. The quantity b is proportional to v or $b = \alpha v$. The expression $\psi_1(T, \rho)$ may therefore be written $D\left(1 + a\frac{\rho}{\rho_c}\right)\rho$, where D is a function of the temperature and equal to $\frac{RT}{m_1(1-\alpha)}$. Inserting the above expression for $\psi_1(T, \rho)$ in equation (5) and applying the critical point conditions we obtain $D_c = 3p_c v_c$ and $a = 1{\cdot}5$. The average velocity is therefore approximately given by $V_g\left(1 + 1{\cdot}5\frac{\rho}{\rho_c}\right)$. The average velocity of a molecule in a liquid at the critical state is thus about 2·5 times its velocity in the gaseous state.

* *Phil. Mag.* Sept. 1912; *Proc. Camb. Phil. Soc.* Vol. xvi. Pt vii. p. 641.

On the number of α-particles expelled when an atom of Thorium Emanation disintegrates. By JOHN SATTERLY, D.Sc., M.A., St John's College, Lecturer in Physics in the University of Toronto. (Communicated by Professor Sir J. J. Thomson.)

[*Received* 9 August 1912.]

I. *Introductory.*

Until quite recently it was supposed to be true without exception that all the radioactive products which expelled α-particles during disintegration expelled only one α-particle per atom disintegrating.

It was proved to be true in the case of Radium by Rutherford and Geiger and by others who counted the number of α-particles emitted and also measured the volume of helium which accumulated when a known quantity of Radium was under examination.

In the case of Thorium Emanation however an account of some experiments was published in *Le Radium* of Oct. 1911*, by Miss M. Leslie, the interpretation of which suggested that Thorium Emanation gave out four α-particles per atom when it became Th. A.

The author has attacked the problem by comparing the ionising powers of quantities of Radium Emanation and Thorium Emanation which are in equilibrium with known amounts of Radium and Thorium. From a knowledge of the rates at which disintegration proceeds and the ionising powers of the various streams of α-particles it is possible to find the ratio of the number of α-particles expelled per atom of Radium Emanation disintegrating to the number of α-particles expelled per atom of Thorium Emanation disintegrating.

When Radium Emanation is passed into an ionisation vessel the initial leak observed (the air leak of course deducted) is due solely to the change from Emanation to Rad. A. As time goes on Rad. A, Rad. B, Rad. C, etc. grow and decay and the leak increases for a while. The curve of growth of leak is however easily analysed so that although the initial leak is not easily measured it can readily be calculated.

In the case of Thorium Emanation the decay is much more rapid. The first product Th. A has however such an extremely short life that in less than a second it practically attains equilibrium with the Emanation so that the initial leak is due to the two changes, (*a*) Thorium Emanation becoming Th. A and

* See also Barratt, *Le Radium*, March 1912.

(*b*) Th. A becoming Th. B. As time goes on Th. C begins to grow but its ionising power is practically negligible in comparison with the Emanation and Th. A. The leak due to the Emanation and Th. A rapidly decays—it drops to half-value in one minute—but it is possible by taking careful readings to draw a curve and find the initial leak due to them.

II. *Calculation of the relative ionising powers of the amounts of Radium and Thorium Emanations (including Th. A) in equilibrium with known quantities of Radium and Thorium.*

Let N_R be the mass of the known quantity of Radium, λ_R the radioactive constant of Radium, N_r the mass of Radium Emanation in equilibrium with this Radium, and λ_r its constant of change. When in radioactive equilibrium there is equality of rates of change; hence we have

$$\lambda_R N_R = \lambda_r N_r \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

If each atom of Radium Emanation gives out p α-particles when it becomes an atom of Rad. A, and each of these α-particles produces l ions in air under ordinary conditions, the ionising power of the Emanation may be written

$$I_r = \lambda_r N_r p l \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2),$$

from which we get

$$I_r = \lambda_R N_R p l \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3).$$

In the same way we may find the ionising power of Thorium Emanation (and Th. A). Let N_T be the mass of Thorium taken, N_t and N_{tA} the quantity of Emanation and Th. A respectively in equilibrium with it and λ_T, λ_t, λ_{tA} the radioactive constants of Thorium, Thorium Emanation and Th. A. Then as before

$$\lambda_T N_T = \lambda_t N_t = \lambda_{tA} N_{tA} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4).$$

If each atom of Thorium Emanation and Th. A gives q and r α-particles per second respectively when disintegration occurs and an α-particle from Thorium Emanation makes m ions and an α-particle from Th. A makes n ions in air under ordinary conditions, we have for the ionising power of the Emanation and Th. A

$$\begin{aligned} I_t &= \lambda_t N_t q m + \lambda_{tA} N_{tA} r n \\ &= \lambda_T N_T (q m + r n) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5). \end{aligned}$$

Therefore the ratio of the ionising powers of the quantities of Radium and Thorium Emanations in equilibrium respectively with N_R gms. of Radium and N_T gms. of Thorium is given by

$$\frac{I_R}{I_T} = \frac{\lambda_R N_R p l}{\lambda_T N_T (q m + r n)} \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

We may simplify this relation by substituting for λ_R, N_R, λ_T, N_T, p, q, and r their known values.

The writer is not aware of any determination of q and r. The value of p has been determined by Geiger*. It is 174,000. Geiger also determined the number of ions produced by the α-particles from Rad. A and Rad. C. From these data a curve may be plotted between the number of ions produced by the α-particles and their ranges in air under ordinary conditions. Now the ranges of the α-particles from Thorium Emanation and Th. A have been determined by Barratt†. From these ranges and the curve obtained from the Radium products the values of q and r have been deduced. They are 191,000 and 199,000 respectively.

Also $$\lambda_R = 1{\cdot}1 \times 10^{-11},$$

and $$\lambda_T = {\cdot}7 \times 10^{-18},$$

and in the author's experiments

$$N_R = {\cdot}94 \times 10^{-9} \text{ gm.},$$

and $$N_T = 1{\cdot}23 \times 10^{-2} \text{ gm.},$$

so that equation (6) becomes

$$\frac{I_R}{I_T} = \frac{1{\cdot}1 \times 10^{-11} \times {\cdot}94 \times 10^{-9}}{{\cdot}7 \times 10^{-18} \times 1{\cdot}23 \times 10^{-2}} \cdot \frac{174l}{191m + 199n}$$

$$= \frac{1{\cdot}03}{{\cdot}86} \cdot \frac{174l}{191m + 199n},$$

which without serious error reduces to

$$\frac{I_R}{I_T} = \frac{20l}{19m + 20n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

III. *Experimental Details and Results.*

The apparatus was the same as that employed in several of the author's earlier experiments‡. The testing vessel V (fig. 1) was a tall brass cylinder 40 cms. high and 10 cms. in diameter closed at the ends. There was a central wire electrode W penetrating the upper end and reaching nearly to the bottom of the vessel. This wire was joined to one pair of quadrants of a Dolezalek electrometer E, the other pair of quadrants being earthed. The vessel was maintained at 320 volts and the needle of the electrometer at 80 volts by batteries of small cells. When the wire W was insulated its potential gradually rose and the spot of light moved across a scale about 2 metres away from the

* *Proc. Roy. Soc.* July 1909.
† *Le Radium*, March 1912.
‡ *Phil. Mag.* Oct. 1908, July 1910; *Proc. Camb. Phil. Soc.* Vols. xv, xvi.

mirror. The normal air leak was 1·0 to 1·1 cms. per minute. The sensitiveness of the electrometer was 950 mm. per 1 volt potential difference between the quadrants. The testing vessel was fitted with two side tubes. One communicated to a manometer M and the other, which was used as an inlet and exhaust tube, communicated to a calcium chloride drying tube D.

To get the Radium Emanation from the solution the following method was adopted. The solution was placed in a flask R.

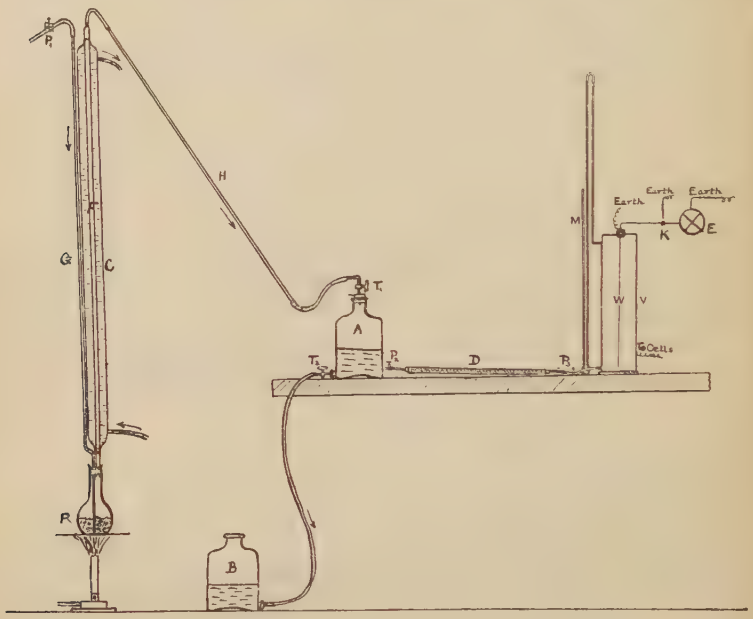

Fig. 1.

Through the cork of this there passed two long tubes about 5 feet long, a wide one F going to a condenser C and a narrow one G ending in an india-rubber tube provided with a clip P_1. The aspirator used for collecting the Radium Emanation consisted of two large bottles A and B joined by tubing, A being provided with taps T_1, T_2.

After the Radium solution had been resting some time the tube F was joined to the bottle A by a tube H, and P_1 being closed the taps T_1, T_2 were opened. The solution was boiled for 30 minutes or so and then P_1 being opened the aspirator drew all the Radium Emanation into A, the water in A being run down to a known mark. Meanwhile the air leak in V was taken. The testing vessel was then exhausted by a water-pump; P_3 closed,

D exhausted and P_2 closed. Communication was then made between D and A and the emanation and air collected in A were passed into V. The leak was taken, as is usual, during the interval from 10 minutes to 20 minutes after filling. This leak, less the air leak, is given in the following table.

TABLE I.

Accumulation of Radium Emanation in a Solution containing $\cdot 94 \times 10^{-9}$ *gm. Radium.*

	Period of rest	Growth of Emanation expressed as leak in cms. per minute	
		In this period (observed)	The equilibrium amount (calculated)
In 1912	72 hours	29·1	69
	$23\frac{1}{2}$ „	11·7	72
In 1910*	$23\frac{3}{4}$ „	11·4	69
	24 „	11·9	72
	$23\frac{3}{4}$ „	11·8	72
			Mean 71

From this mean leak the initial leak, which would have been obtained if the vessel could have been suddenly filled with the equilibrium amount of Emanation, is obtained by multiplying by ·73. The calculation of this factor is given in an earlier paper in these *Proceedings*†.

Thus the initial leak = $\cdot 73 \times 71 = 52$ cms. per minute; i.e. could the Radium Emanation in equilibrium with $\cdot 94 \times 10^{-9}$ gm. Radium have been suddenly passed into my testing vessel the initial leak would have been 52 cms. per minute. This conductivity is due solely to the ionisation accompanying the disintegration of Radium Emanation into Rad. A.

To get the leak due to the Thorium Emanation the arrangement was modified by the omission of the aspirator AB and by the insertion of an ion-catcher‡ between D and V. The Thorium solution is kept boiling for some time, the tube H hanging slack. Equilibrium between the emanation and the solution occurs if a rest of 10 minutes is given between the last clearing out. Then

* See *Proc. Camb. Phil. Soc.* Vol. xv. p. 543.
† *Ibid.* Vol. xvi. pp. 519, 520. ‡ *Ibid.* p. 522.

when V and D have been exhausted H is joined direct to D and the testing vessel filled as quickly as possible by the rush of air through G and the solution. As a rule the vessel was filled in 20 or 25 seconds and readings of the leak could be commenced 30 seconds after the rush of gas started. The leaks were taken as described on p. 523 in my paper on "The quantities of Radium and Thorium Emanations contained in the air of certain soils*." The initial leak due to the Thorium Emanation and Th. A disintegrations was measured on eight occasions; the values obtained are given in the following table.

TABLE II.

Accumulation of Thorium Emanation in a Solution containing $1{\cdot}23 \times 10^{-2}$ *gm. Thorium.*

Initial leak in cms. per minute produced by the equilibrium amount of Emanation
112
112
100
108
116
112
108
102
Mean 108

We have now the data required for the solution of equation (7), for writing

$$I_R = 52,$$

and

$$I_T = 108,$$

we get

$$\frac{52}{108} = \frac{20l}{19m + 20n} \quad \text{.....(8).}$$

Therefore, approximately

$$40l = 19m + 20n,$$

or

$$2l = m + n \text{.....(9).}$$

Rutherford and Geiger showed that l was equal to unity. From this it follows that since m and n are both integral they must both be unity.

* *Proc. Camb. Phil. Soc.* Vol. XVI.

The conclusion is that an atom of Thorium Emanation gives out only one α-particle when it changes to an atom of Th. A and that an atom of Th. A gives out only one α-particle when it becomes an atom of Th. B.

Note 1. The above result was assumed by the author in his paper on "The quantities of Radium and Thorium Emanations contained in the air of certain soils." It is satisfactory to know that the assumption is justified.

Note 2. It has been thought that the emanating power of weak solutions of Radium decreases with time owing to a deposition of Radium or an adsorption of Radium by the glass of the bottle. The agreement of the results of 1910 and 1912 shown in Table I. shows that with slightly acid solutions this does not occur.

Note 3. The author returns his thanks to Prof. E. Rutherford for his gift of the standard Radium Solution, and to Prof. J. Joly for his gift of the standard Thorium Solution. The latter was made from ·1 gm. of Thorianite containing 79 °/₀ Thorium Oxide and 14 °/₀ Uranium Oxide. Some experiments of the author's showed that its Radium content was $\cdot 76 \times 10^{-9}$ gm. Its Thorium content was $1 \cdot 23 \times 10^{-2}$ gm. as stated above.

The above experiments were carried out in the Cavendish Laboratory. On leaving the laboratory after several years' work I desire to express my best thanks to Prof. Sir J. J. Thomson for his unfailing interest and kindly advice at all times.

The Proportions of the sexes in Forficula auricularia. By H. H. Brindley, M.A., St John's College.

[*Read* 20 May 1912.]

It has been known for a long time that the forceps of the male of the common earwig vary in length very considerably, thus de Geer* writing in 1773 stated "Dans quelques mâles j'ai trouvé la pince très-longue, ou de longueur égale avec le ventre." Stephens† made a distinct species under the name of *Forcicula forcipata* to cover the forms in which the male possesses strikingly long forceps. This has not been retained by later authorities (see Fischer‡, Brunner von Wattenwyl§ and Burr‖). The first observation that in some localities the mean length of forceps of the male is rare, while "low" males and "high" males are abundant, was made by Bateson¶ in a collection of 1000 adult earwigs of both sexes made in the Farn Islands by Miss A. Bateson in September, 1892. The curve of variation of the forceps lengths is therefore dimorphic. Since this observation collecting has been carried on in certain other islands and various coast and inland places in the British Isles in the hope of obtaining some light on the extent to which "high" and "low" males occur together, and also to gather some indication as to the factors which influence the dimensions of the forceps. This enquiry is still in progress.

Incidentally the numerical proportions of the sexes in the catches obtained has been recorded in most cases, and in this direction the results are of interest in the considerable extent to which the proportions vary. It should be said that the collections have been quite haphazard, males and females have been captured indifferently. In cases where I have not made the captures myself, the various friends to whom I stand indebted for collections have understood that no choice should be made between the sexes, and other collectors, such as lighthouse keepers and gardeners, have simply been asked to catch as many earwigs as possible.

* "Mémoires pour servir à l'Histoire Naturelle des Insectes," Stockholm, III. 1773, p. 548.

† *British Entomology*, 1835, VI. p. 6, pl. xxviii. fig. 4.

‡ *Orthoptera Europaea*, 1853, p. 74.

§ *Prodr. d. Europ. Orthopt.*, 1882, p. 12.

‖ *Entom. Month. Mag.*, Oct. 1911, XXII. 262, p. 225.

¶ Bateson and Brindley, "On some cases of Variation in Secondary Sexual characters statistically examined," *Proc. Zool. Soc. Lond.*, Nov. 15, 1892, p. 585.

Locality	Date	♂ and ♀ adults	centage of males	Soil, etc.
Round Island, Scilly Isles	Aug., Sept., 1911	3655	16·1	Granite rocks.
Ilkley, Yorks.	Aug., Sept., 1911	333	20·4	Sandy gardens, dahlias, tropaeolums.
Frinton-on-Sea, Essex	Aug., Sept., 1901	79	32·9	Heavy loam.
Shelford, Cambs.	July, Aug., 1893	3336	32·9	Chalky gardens.
Bobbing, Kent	Aug., Sept., 1906	799	33·7	Gardens with light loam on gravel.
Rannerdale, Cumb.	Aug., Sept., 1903	326	35·8	300 ft. alt., slate stones, dahlias, rhubarb, convolvulus.
Longniddry, E. Lothian	Aug., Sept., 1901	217	35·9	Loam.
Bobbing, Kent	Sept., 1903	1336	36·1	Gardens with light loam on gravel.
Sedbergh, Yorks.	Aug., Sept., 1903	307	36·1	Gravel garden, dahlias, beehives.
Ipswich, Suffolk	Aug., Sept., 1903	477	37·1	Light, sandy; dahlias, phloxes, sunflowers.
Parkstone, Dorset	Aug., Sept., 1901	263	37·3	Sandy, poor soil.
Chesterton, Cambs.	July, Aug., 1904	152	38·1	Clay and gravel.
Shenstone, Staffs.	Aug., Sept., 1901	747	38·3	Loam on gravel.
Beal, Northumberland	Aug., Sept., 1901	198	38·4	Clay, added lime, dahlias.
Goathorn, Poole Harbour, Dorset	Aug., Sept., 1911	370	38·4	Sandy, loam in kitchen garden.
Brownsea, Poole Harbour, Dorset	Aug., Sept., 1911	353	38·5	Sandy, poor soil.
Whirlow, Yorks.	Aug., Sept., 1903	475	38·9	700 ft. alt., stones and clay, kitchen garden, dahlias.
Clare Island, Co. Mayo	Aug. 22–24, 1909	112	40·2	Limestone, uncultivated, under stones on very short grass.
Shelford, Cambs.	July, Aug., 1894	2763	41·1	Chalky gardens.
Inner Farn Island, Northumberland	Oct. 3, 1907	308	41·2	Stony, grass, poultry field.
Poulton-le-Fylde, Lancs.	Aug., Sept., 1901	2656	42·8	Loamy.
Bobbing, Kent	Aug., Sept., 1904	654	42·9	Gardens with light loam on gravel.
Brownsea, Poole Harbour, Dorset	Aug., Sept., 1910	103	43·7	Sandy, poor soil.
Budle Bay, Northumberland	Aug., Sept., 1903	1115	44·4	Sandy, close to sea shore, grass, ragwort.
Black Torrington, N. Devon	Aug., Sept., 1902	1163	45·0	Clay, cow parsley, woody district.
Histon, Cambs.	Aug., 1894	3564	46·1	Clay, gravel.
Greater Cumbrae, Bute	July, Aug., 1911	224	46·4	Gardens 10—20 ft. alt., close to moorland 100—250 ft. alt.
Godalming, Surrey	July, Aug., 1912	1205	46·6	Garden and adjoining field, sandy soil over Lower Greensand.
Stanhope, Durham	Aug., Sept., 1901	1307	49·6	Gravel on limestone.
Hilbre Island, Cheshire	Sept. 23, 1910	69	53·6	Sandstone, low, wet.
Widerperns, Farn Islands, Northumberland	Oct. 4, 1907	2654	53·6	Rocky, under stones on grass and *Silene maritima*.
Colonsay, Argyllshire	Aug., Sept., 1903	170	55·8	Stony.
Widerperns, Farn Islands*	Sept. 12, 1892	1000	58·3	Rocky, under stones on grass and *Silene maritima*.
Tresco, Scilly Isles	Aug., Sept., 1911	330	59·7	Granite, gardens.

* Bateson, *loc. cit.*

The preceding table gives the results obtained from collections in which the sexes were counted. One or two cases of collections of less than 100 (printed in italics) are included, but these are too small to be more than indications of how the proportions of the sexes might be expected to work out in large captures.

I am indebted to Mr E. J. Burgess Sopp, F.E.S., for the following particulars of captures made by him, some of which have been published*, while the others, which have so far not been printed, he has kindly allowed me to include in the table below.

Locality	Date	Total ♂ and ♀ adults	Percentage of males	Soil, etc.
Southport, Lancs.	1903	129	32·6	Sand dunes.
Hilbre Island, Cheshire	Aug., 1903	118	44·1	Sandstone, low, wet.
Birkdale, Lancs.....	1903	400	44·5	Gardens.
Brownsea, Poole Harbour, Dorset ...	Aug., 1903	83	45·8	Sandy, poor soil.
Southport, Lancs.	1904	236	46·2	Sand dunes.
Tresco, Scilly Isles ...	Aug., 1903	146	55·5	Granite, gardens.

It will be seen that while as a rule the females exceed the males by about 10 per cent., there are considerable differences in the proportions of the sexes in different localities, and also in collections made in the same locality in different years. There is some suggestion that males are more numerous on islands, but Round Island, Scilly, is a striking contradiction. The collection made there last year shows the lowest proportion of males observed so far, and it is curious that the highest is from another of the Scilly Isles, Tresco, which is only a mile from Round Island. This case of great difference between the percentages (43·6) calls attention to the possibility of the conditions of life affecting the proportion of the sexes: Round Island is a small mass of granite, while the specimens from the much larger island of Tresco were caught in the Abbey Gardens.

On the other hand, the two collections made in 1911 from localities in Poole Harbour show identical percentages of males. Brownsea is an island and Goathorn Point on the mainland was chosen for a collection in the same month, as it is one of the nearest places to Brownsea—the distance is three-quarters of a mile. Brownsea is a partially cultivated island about 4 miles in circumference, and in soil and vegetation it is quite similar to

* Sopp, "The Callipers of Earwigs," *Proc. Lanc. and Ches. Ent. Soc.*, 1904, p. 38.

Goathorn. In these two instances of the Scilly Islands and Poole Harbour we have a great difference in the sex proportions in two neighbouring localities with very different physical features and identity of the proportions in two neighbouring localities of the same physical nature. But a collection from Brownsea, unfortunately rather small, made in 1910 gave a decidedly higher percentage of males, viz. 43·7 instead of 38·5. In that year no collection was made at Goathorn, so no comparison with that spot can be made for 1910. But what is said here is offered only as the barest suggestion that the physical features of a locality may influence the proportions of the sexes. The instances quoted may be mere coincidences and the percentage of males be due to quite other causes. The particulars given in the above table do not justify any stress being laid for the present on the characters of the soil or vegetation as likely to influence the proportions of the sexes.

Moreover, regard must be paid to the variation in the percentages of males from the same locality in different years.—Thus the catches from Bobbing show a range of 9·2, Shelford, 8·2, and the Farn Islands, 4·7. In all these the collections were made from the same garden or other spot in the different years and the totals obtained were sufficiently large to place reliance on the percentages, and it seems clear that the sex proportions do vary considerably even in successive years. There is at present no explanation of this. It should be said that all the collections were made in months when nearly all the individuals found were adults, thus the results were not influenced by the possibility that males reach maturity sooner than females or *vice versa*. This year I have kept in captivity a number of young earwigs kindly collected for me by Mr L. Doncaster in his garden in Cambridge. On May 24 the body length of most of them was 5 mm. By August 1st, all the survivors were adults (there were not many deaths and the insects throve on leaves and flowers of *Tropæolum*, which they ate greedily and in preference to any other plant offered to them*).

That the adult female does so normally seems certain, for we know from de Geer†, Taschenberg‡, Camerano§, Rühl‖,

* In a collection kindly made for me by Mr Oswald Latter at Godalming in the latter half of July and the first half of August this year (since this paper was read to the Society), there were only 118 immature individuals in a total catch of 1323.

† *loc. cit.*

‡ In Brehm, "Merveilles de la Nature, Les Insectes," etc.; édit. franç. par J. Künckel d'Herculais, t. I. p. 394.

§ *Boll. d. Soc. Entom. Ital.*, 1880, p. 46.

‖ *Mittheil. der Schweizer. Entomol. Gesellsch.*; *Bull. d. l. Soc. Entom. Suisse*, VII. 1887, p. 311.

Larbelétrier*, Lesne† and others that the female is found in the first half of the year guarding her eggs.

It appears that there is a considerable range in the times of oviposition and hatching. The accounts of the authors quoted above mention females found with their eggs or in the act of laying them from January to May inclusive, and females found with quite young individuals from January to June inclusive. It is possible that the character of the season is a factor controlling oviposition. Camerano‡ states that it remains uncertain whether the female lays in autumn or spring. He doubts if the fact of having found eggs in January is sufficient evidence that they are laid normally in the autumn, because the preceding autumn (1876) had been comparatively fine and warm. On October 4th, 1907, F. A. Potts and myself obtained a large number of earwigs on the Widerperns in the Farn Islands and brought them alive to Cambridge. In about a fortnight numbers of the females had laid their eggs, a result we are inclined to attribute to keeping the insects in the Zoological Laboratory, where the temperature is much higher than that of the Farn Islands in October. Unfortunately neither the adults nor the eggs survived long, for the insects were soon covered with Gamasid mites, the young of which we imagine must have been brought in the soil which was obtained with the earwigs. In the following October we obtained another catch from the same islets and kept them in the open on the roof of the Laboratory. These remained free from mites and most of them laid eggs in November, but in no case were they hatched. The females and eggs were kept in plaster of Paris cells, but though special precautions were taken to prevent undue evaporation on the one hand, and too much humidity on the other, the eggs either dried up or were destroyed by mould.

In view of the possible influence of temperature and the character of the season on oviposition it seems not impossible that the same causes may affect the survival of males through the winter. I am unable to find any statements on the normal length of life of earwigs in the writings I have mentioned. There is no doubt that adult males are found comparatively rarely in the early months of the year, but I have come across them towards the end of winter in gardens in Cambridge. Camerano§ mentions having found a living male in January in the South of Europe. He placed this male and two females with some eggs laid by one of the latter under an inverted glass, and observed

* *La Nature*, 5 juillet, 1890, p. 75.

† Quoted by H. Gadeau de Kerville in "Note sur l'accouplement, les œufs et l'amour maternel des Forficulidés," Rouen, 1907, p. 18, in which extracts from the above papers are given also. See also Sharp, *Camb. Nat. Hist.* v. pp. 212—214.

‡ *loc. cit.*

§ *loc. cit.*

that only the female who had laid showed any interest in the eggs, collecting them when they were purposely scattered. I know of no statement that the male earwig watches the eggs as it is known the female does.

It is hoped to continue observation on the points considered in this paper: all that can be said at present is that (i) the proportions of the sexes differ considerably in different localities in the same year and sometimes differ considerably in localities quite near each other, (ii) the proportions may differ appreciably in the same locality in different years, (iii) the extent to which males survive the winter very likely varies, and if this is so we have a factor affecting (ii), (iv) there is a slight suggestion that the percentage of males is higher on small islands, (v) the evidence that the characters of the soil or vegetation or altitude affect the proportions of the sexes is exceedingly slight.

PROCEEDINGS AT THE MEETINGS HELD DURING THE SESSION 1911—1912.

ANNUAL GENERAL MEETING.

October 30th, 1911.

In the Comparative Anatomy Lecture Room.

Prof. Sir George Darwin, President, in the Chair.

The following were elected Officers for the ensuing year:

President:

Prof. Sir George Darwin.

Vice-Presidents:

Prof. Newall.
Prof. Hopkinson.
Prof. Wood.

Treasurer:

Prof. Hobson.

Secretaries:

Rev. Dr Barnes.
Mr A. Wood.
Mr F. A. Potts.

Other Members of the Council:

Prof. Sir J. Larmor.
Prof. Biffen.
Prof. Pope.
Mr R. H. Rastall.
Dr Keith Lucas.
Dr E. A. Newell Arber.
Prof. Sir J. J. Thomson.
Mr J. E. Purvis.
The Master of Christ's.
Mr R. P. Gregory.
Dr Cobbett.
Mr J. Mercer.

The following was elected a Fellow of the Society:

C. E. Moss, B.A., Emmanuel College.

The following were elected Associates:

J. E. Bowen, Trinity College.
N. Bohr, Trinity College.
F. P. Kerschbaum, Gonville and Caius College.

The following Communications were made:

1. Note on the mode of discharge of the Cuverian organs of *Holothuria nigra*. By G. R. Mines, M.A., Sidney Sussex College.

2. The Discharge of Spermatozoa by *Unio pictorum*. By Oswald H. Latter. (Communicated by Dr Shipley.)

November 13*th*, 1911.

In the Cavendish Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following Communications were made:

1. Application of positive rays to the study of chemical problems. By Professor Sir J. J. Thomson.

2. Electron theory of metals. By N. Bohr, Trinity College. (Communicated by Professor Sir J. J. Thomson.)

3. Secondary characteristic Röntgen Radiation from Elements of High Atomic Weight. By J. C. Chapman, Gonville and Caius College. (Communicated by Professor Sir J. J. Thomson.)

November 27*th*, 1911.

In the Comparative Anatomy Lecture Room.

Dr Shipley, Master of Christ's College, in the Chair.

The following were elected Fellows of the Society:

A. J. Berry, B.A., Downing College.
S. T. Burfield, B.A., Selwyn College.
H. B. Fantham, B.A., Christ's College.
R. D. Kleeman, B.A., Emmanuel College.
A. E. Oxley, B.A., Trinity College.
G. Stead, B.A., Clare College.

The following Communications were made:

1. A new type of parasitism in the Polychaeta. By F. A. Potts, M.A., Trinity Hall.

2. On the Experimental Hybridisation of Echinoids. By Messrs Shearer, Fuchs, Doncaster and Gray.

(1) General account of the Experiments (Mr C. Shearer). Illustrated with lantern slides.

(2) The Chemical control of inheritance in Echinoid Hybrids (H. M. Fuchs).

(3) Cytological observations of Hybrid Echinoid Eggs (Mr L. Doncaster and J. Gray).

3. Note on the condensation of tryptophane with certain aldehydes. By Miss A. Homer. (Communicated by Mr F. G. Hopkins.)

January 29th, 1912.

In the New Medical Schools.

Professor Sir George Darwin, President, in the Chair.

The following were elected Fellows of the Society:

R. Whiddington, B.A., St John's College.
W. A. R. Wilks, M.A., Gonville and Caius College.

The following Communications were made:

1. Demonstration of a Stereotaxic Instrument for directing insulated or other needles to any desired point in an animal's brain by graduated movement in three planes. By R. H. Clarke. (Communicated by Dr Shipley.)

2. Observations on Fowl pest. By E. Hindle, Magdalene College. (Communicated by Professor Nuttall.)

3. Gregarines in Rat-fleas. By C. Strickland, M.A., Gonville and Caius College. (Communicated by Professor Nuttall.)

4. On the toxicity of serum. By Major Cornwall. (Communicated by Professor Nuttall.)

5. The genus *Rhipicephalus*. By C. Warburton, M.A., Christ's College.

6. The parasites of equine biliary fever. By Professor Nuttall.

February 12th, 1912.

In the Cavendish Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following were elected Fellows of the Society:

Harold Ackroyd, M.D., Gonville and Caius College.
H. Rottenburg, M.A., King's College.

The following was elected an Associate:

A. N. Shaw, Gonville and Caius College.

The following Communications were made:

1. On the Existence of a Polymeric Modification of Hydrogen. By Professor Thomson.

2. An Experiment to illustrate the Mechanical Tension on the Surface of a Charged Conductor. By E. F. Burton, B.A.

3. Radio-activity and Molecular Structure. By W. A. D. Rudge, M.A., St John's College.

4. On the double-six which admits a group of 120 collineations into itself. By W. Burnside, M.A., Pembroke College.

5. A Magnetic Examination of the Function of the Water Molecule in certain Dilute Solutions. By A. E. Oxley, B.A., Trinity College.

February 26th, 1912.

In the Botany School.

Dr Shipley, Master of Christ's College, in the Chair.

The following were elected Fellows of the Society:

E. Rutherford, B.A., Trinity College.
C. G. Darwin, B.A., Trinity College.

The following were elected Associates:

E. N. da C. Andrade, Emmanuel College.
S. E. Sheppard, Emmanuel College.

The following Communications were made:

1. The Chromosomes in the oogenesis and spermatogenesis of the white Butterfly *Pieris brassicae*. By L. Doncaster, M.A., King's College.

2. Preliminary note on the occurrence of living bacteria in the organs and blood of normal animals. By Dr Cobbett.

3. Some Observations with the Ultramicroscope on Plant Cells. By S. R. Price, B.A., Clare College. (Communicated by Professor Seward.)

4. Rhizopods from the Carboniferous Period (illustrated with Lantern slides). By R. C. McLean. (Communicated by Professor Seward.)

5. The Chromosomes of a giant form of *Primula sinensis*. By R. P. Gregory, M.A., St John's College.

March 11th, 1912.

In the Chemical Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following was elected a Fellow of the Society:

R. H. Fowler, B.A., Trinity College.

The following Communications were made:

1. Resolution of Racemic Benzoylalanine. By Professor Pope and C. S. Gibson, M.A., Sidney Sussex College.

2. The optically active hydroxyhydrindamines. By Professor Pope and Mr J. Read.

3. The Boiling points of Zinc, Cadmium, Mercury, Sodium, Potassium, and their alteration with change of pressure. By C. T. Heycock, M.A., King's College, and F. E. E. Lamplough, M.A., Trinity College.

4. The metastable condition of undercooling in metals. By F. E. E. Lamplough, M.A., Trinity College.

5. The quantities of Radium and Thorium Emanations contained in the air of Soils. By J. Satterly, M.A., St John's College. (Communicated by Professor Sir J. J. Thomson.)

6. On a theory of the dissymmetrical distribution of secondary Röntgen Radiation. By J. A. Crowther, M.A., St John's College.

7. The Variation of Magnetic Susceptibility with Temperature. By A. E. Oxley, B.A., Trinity College.

8. The Coagulation of Colloidal Copper. Rate of Coagulation. By H. H. Paine, M.A., Trinity College.

9. On the Different Internal Energies of a Substance. I. By R. D. Kleeman, B.A., Emmanuel College.

May 6th, 1912.

In the Cavendish Laboratory.

Professor Sir George Darwin, President, in the Chair.

The following were elected Fellows of the Society:

T. Shirley Hele, M.D., Emmanuel College.
S. R. Price, B.A., Clare College.

The following Communications were made:

1. On the Unit Theory of Radiation. By Professor Sir J. J. Thomson.

2. A simple viscometer for very viscous liquids. By G. F. C. Searle, ScD., Peterhouse.

3. The action of Sunlight and of Radium Salts on Glass. By W. A. D. Rudge, M.A., St John's College.

4. On the Different Internal Energies of a Substance. II. By R. D. Kleeman, B.A., Emmanuel College.

5. The Detection of small amounts of Polarisation in Light from a Dull Sky. By A. E. Oxley, B.A., Trinity College.

6. An attempt to Refract Röntgen Radiation. By J. C. Chapman, Gonville and Caius College. (Communicated by Professor Sir J. J. Thomson.)

7. (1) The Problem of Derangement in the Theory of Permutations. (2) On Compound Denumeration. By Major P. A. MacMahon.

May 20th, 1912.

In the Comparative Anatomy Lecture Room.

Professor Seward in the Chair.

The following was elected an Associate of the Society:

H. A. McTaggart, Fitzwilliam Hall.

The following Communications were made:

1. An Experiment on Rabbits. By Professor PUNNETT.

2. Proportions of the sexes in *Forficula auricularia*. By H. H. BRINDLEY, M.A., St John's College.

3. *Stachypteris Hallei*: A new Jurassic Fern. (Illustrated with Lantern slides.) By H. H. THOMAS, M.A., Downing College.

4. Some observations on electrocardiograms of cold blooded animals. (Illustrated with Lantern slides.) By G. R. MINES, M.A., Sidney Sussex College.

5. The Structure and Homology of the Microsporidian Spore, as seen in *Nosema apis*. By H. B. FANTHAM, B.A., Christ's College, and Miss ANNIE PORTER.

6. Cyclic Paths for Rays reflected at an Elliptical Boundary. By R. HARGREAVES, M.A., St John's College.

7. Note on the Spectrum of argon. By G. STEAD, B.A., Clare College.

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